NEW HIERARCHIC THEORY OF CONDENSED MATTER AND ITS COMPUTERIZED APPLICATION TO WATER & ICE

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This work contains review of original quantum Hierarchic theory of condensed matter, general for liquids and solids and its numerous branches. Computer program (copyright, 1997, Kaivarainen), based on new theory, was used for comprehensive simulations of water and ice physical properties.

Condensed matter is considered as gas of 3D standing waves (collective excitations) of different nature: thermal de Broglie waves (waves B), IR photons and thermal phonons. Quantitative interrelation between microscopic, mesoscopic (as intermediate) and macroscopic properties of condensed matter are demonstrated. New theories of total internal energy, including contributions of kinetic and potential energy, heat capacity, surface tension, vapor pressure, thermal conductivity, viscosity and self-diffusion are described. Hierarchic theory of osmotic pressure, based on new state equation, new theories of light refraction, Brillouin light scattering and Mössbauer effect are presented also in article and compared with available experimental data for water and ice. Lot of hidden parameters, inaccessible for experiment, describing the dynamic and spatial properties of 24 quantum collective excitations of matter, can be calculated also, as demonstrated on examples of water and ice.

Total number of physical parameters of liquids and solids in wide T-interval, including that of phase transitions, to be possible to evaluate using CAMP computer program, is about 300.

The agreement between theoretical and available experimental results is very good. The evidence of high-T mesoscopic molecular Bose condensation (BC) in water and ice in form of coherent clusters is obtained. The new mechanisms of the 1st and 2nd order phase transitions, related to such clusters formation/melting, their assembly/disassembly and symmetry change is proposed.

Theory unifies dynamics and thermodynamics on microscopic, mesoscopic and macroscopic scales in terms of quantum physics. The idea of new optoacoustic device: Comprehensive Analyzer of Matter Properties (CAMP) with huge informational possibilities, based on computer program, elaborated and its multisided applications are described. This work may be considered as a theoretical part of MANUEL to CAMP - program. The computer program (CAMP) is applicable for any condensed matter, if primary four experimental parameters are known in the same T-interval. It may be ordered from the author.

The number of articles, devoted to different aspects and possibilities of new theory see at the electronic journal "Archive of Los-Alamos": http://arXiv.org/find/cond-mat,physics/1/au:+kaivarainen_A/0/1/past/0/1

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1. INTRODUCTION

A quantum and quantitative theory of liquid state, as well as a general theory of condensed matter, was absent till now. This fundamental problem is crucial for different brunches of science and technology. The existing solid states theories did not allow to extrapolate them successfully to liquids.

Widely used molecular dynamics method is based on classical approach and corresponding computer simulations. It cannot be considered as a general one. The understanding of hierarchic organization of matter and developing of general theory needs a mesoscopic bridge between microscopic and macroscopic physics, between liquids and solids.

The biggest part of molecules of solids and liquids did not follow classical Maxwell-Boltzmann distribution. This means that only quantum approach is valid for elaboration of general theory of condensed matter.

Our theoretical study of **water and aqueous systems** was initiated in 1986. It was stimulated by necessity to explain the nontrivial phenomena, obtained by different physical methods in our investigations of water-protein solutions. For example, the temperature anomalies in water physical properties, correlating with changes in large scale protein dynamics were found in our group by specially elaborated experimental approaches (Kaivarainen, 1985). It becomes evident, that the water clusters and water hierarchical cooperative properties are dominating factors in self-organization, function and evolution of biosystems. The living organisms are strongly dependent on water properties, representing about 70% of the body mass. On the other hand, due to its numerous anomalies, water is an ideal system for testing a new theory of condensed matter. If the theory works well with respect to water and ice, it is very probable, that it is valid for other liquids, glasses or crystals as well. For this reason we have made the quantitative verification of our hierarchic concept (Kaivarainen, 1989, 1992, 1995, 1996, 2000) on examples of water and ice.

Our theory considers two main types of molecular heat motion: *translational (tr)* and *librational (lb) anharmonic* oscillations, which are characterized by certain distributions in three- dimensional (3D) impulse space. The most probable impulse or momentum (p) determine the *most probable* de Broglie wave (wave B) length ($\lambda_B = h/p = v_{ph}/\nu_B$) and phase velocity ($v_{ph}$). Conformational intramolecular dynamics is taken into account indirectly, as far it has an influence on the intermolecular dynamics and parameters of waves B in condensed matter. Solids and liquids are considered as a hierarchical system of collective excitations - metastable quasiparticles of the four new type: **effectons, transitons, convertons and deformons,** strongly interrelated with each other.

When the length of standing waves B of molecules exceed the distances between them, then the coherent molecular clusters may appear as a result of high temperature molecular Bose-condensation (BC). The possibility of BC in liquids and solids at the ambient temperatures is one of the most important results of our model, confirmed by computer simulations. Such BC is mesoscopic one, in contrast to macroscopic BC, responsible for superfluidity and superconductivity. The value of the standing *wave B* length, which determine the edges of the primary effecton (tr or lb) in selected directions (1,2,3) may be considered as a *mesoscopic parameter of order.*

The primary *transitons* and *convertons* have common features with *coherent dissipative structures* introduced by Chatzidimitrov-Dreisman and Brändas in

1988. Such structures were predicted on the background of complex scaling method and Prigogin theory of star- unitary transformations.

Estimated from principle of uncertainty, the minimum boson's "degrees of freedom"($n_{\min}$) in these spontaneous coherent structures are equal to:

$$n_{\min} \geq \tau(2\pi k_B T/h) \tag{1.1}$$

where τ is relaxation time of coherent-dissipative structures.

If, for example, $\tau \simeq 10^{-12}c$, corresponding to excitation of a molecular system by infrared photon, then at $T = 300K$ one get $n_{\min} \simeq 250$. It means that at least 250 degrees of freedom, i.e. [250/6] molecules, able to translations and librations act **coherently** and produce a photon absorption/emission phenomenon. The traditional consideration of an oscillating individual molecule as a source of photons is replaced by the notion of a *correlation pattern* in such a model.

The interaction between atoms and molecules in condensed matter is much stronger and thermal mobility/impulse much lesser, than in gas phase. It means that the temperature of Bose condensation can be much higher in solids and liquids than in the gas phase. **The lesser is interaction between molecules or atoms the lower temperature is necessary for initiation of Bose condensation.**

This is confirmed in 1995 by Ketterle's group in MIT and later by few other groups, showing the Bose-Einstein condensation in gas of neutral atoms, like sodium (MIT), rubidium (JILA) and lithium (Rice University) at very low temperatures, less than one Kelvin. However, at this temperatures the number of atoms in the primary effectons (Bose condensate) was about 20,000 and the dimensions were almost macroscopic: about 15 micrometers.

For comparison, the number of water molecules in primary librational effecton (coherent cluster), resulting from mesoscopic BC at freezing point 273 ^{0}K is only 280 and the edge length about 20 Å (see Fig. 7).

Our **Hierarchic theory of matter** unites and extends strongly two earlier existing most general models of solid state (Ashkroft and Mermin, 1976):

a) the Einstein model of condensed matter as a system of independent quantum oscillators;

b) the Debye model, taking into account only collective phenomena - phonons in a solid body as in continuous medium.

Among earlier models of liquid state the model of flickering clusters by Frank and Wen (1957) is closest of all to our model. In our days the quantum field theoretical approach to description of biosystems with some ideas, close to our ones has been developed intensively by Umesawa's group (Umezawa, et. al., 1982; Umezawa, 1993) and Italian group (Del Giudice, et al., 1983; 1988, 1989).

Arani et al. introduced at 1998 the notion of Coherence Domains (CD), where molecules are orchestrated by the internal electromagnetic waves (IR photons) of matter [13]. This idea is close to our notion of collective excitations of condensed matter in the volumes of 3D translational and librational IR photons, termed primary electromagnetic deformons (see next section).

The new physical ideas required a new terminology. It is a reason why one can feel certain discomfort at the beginning of reading this work. To

facilitate this process, we present below a description of a new quasiparticles, notions and terms, introduced in our Hierarchic Theory of matter (see Table 1). Most of notions and properties, presented below are not postulated, but a results of our computer simulations.

2. THE NEW EXCITATIONS, INTRODUCED IN HIERARCHIC THEORY OF MATTER AND THEIR PROPERTIES

The Most Probable (primary) de Broglie Wave (wave B)

The main dynamics of particles in condensed matter (liquid or solid) represents thermal anharmonic oscillations of two types: *translational* (tr) and *librational* (lb). The corresponding length of the most probable wave B of molecule or atom of condensed matter can be estimated by two following ways:

$$[\lambda_{1,2,3} = h/mv_{gr}^{1,2,3} = v_{ph}^{1,2,3}/\nu_B^{1,2,3}]_{tr,lb} \tag{2.1}$$

where the most probable impulse (momentum): $p^{1,2,3} = mv_{gr}^{1,2,3}$ is equal to product of the particle mass (m) and most probable group velocity ($v_{gr}^{1,2,3}$). We prefer to use term *impulse*, instead *momentum,* for the end not to confuse the latter notion with *momentum of impulse,* defined as:

$$mv_{gr}^{1,2,3}\lambda_{1,2,3} = h \tag{2.1a}$$

The length of wave B could be evaluated, as the ratio of Plank constant to impulse and as the ration of most probable phase velocity $(v_{ph}^{1,2,3})_{tr,lb}$ to most probable frequency $(\nu_B^{1,2,3})_{tr,lb}$. The indices (1,2,3) correspond to selected directions of motion in 3D space, related to the main axes of the molecules symmetry and their tensor of polarizability. In the case when molecular motion is anisotropic one, we have:

$$\lambda_1 \neq \lambda_2 \neq \lambda_3 \tag{2.2}$$

It is demonstrated in our work, using Virial theorem (see eqs. 4.10 - 4.14), that due to anharmonicity of oscillations - the most probable kinetic energy of molecules $(T_{\rm kin})_{tr,\,lb}$ is lesser than potential one $(V)_{tr,\,lb}$:

$$(mv^2/2) < (kT/2)$$

where most probable (mean) velocity of particle of matter is equal to corresponding group velocity ($v = v_{gr}$). Consequently, the most probable 3D wave B length is big enough:

$$\left(\frac{V_0}{N_0}\right)^{1/3} < \lambda_{1,2,3} > h/(mk_BT)^{1/2} \tag{2.2a}$$

It is a condition of mesoscopic molecular Bose condensation (BC).

The Most Probable (Primary) Effectons (tr and lb)

A new type of quasiparticles (excitations), introduced as 3D superposition of three most probable pairs of standing waves B of molecules, are termed **primary effectons**. The shape of primary effectons in a general case can be approximated by parallelepiped, with the length of edges determined by 3 most probable standing waves B. The volume of primary effectons is equal to:

$$V_{ef} = (9/4\pi)\lambda_1\lambda_2\lambda_3. \tag{2.3}$$

The number of molecules or atoms forming effectons is:

$$n_m = (V_{ef})/(V_0/N_0), \tag{2.4}$$

where V_0 and N_0 are molar volume and Avogadro number, correspondingly. The n_m increases, when temperature is decreasing and may be about hundreds in liquids or even thousands in solids, as shown in our work.

In liquids, primary effectons may be registered as a clusters and in solids as domains or microcrystalline.

The thermal oscillations in the volume of corresponding effectons are synchronized. It means the coherence of the most probable wave B of molecules and their wave functions. We consider the **primary effectons as a result of partial Bose condensation** of molecules of condensed matter. Primary effectons correspond to the main state of Bose-condensate with the packing number $n_p = 0$, i.e. with the resulting impulse equal to zero.

Primary effectons (librational in liquids and librational and translational in solids), as a coherent clusters, represent self-organization of condensed matter on mesoscopic level, like I. Prigogin dissipative structures. However, revealed in our work mesoscopic high - T Bose condensation, is a quantum phenomenon. It is important to note, that the coherent oscillations of molecules in the volume of the effectons can not be considered as ***phonons (acoustic waves)****, because they are not accompanied by fluctuation of density in contrast to secondary deformons (see below).*

"Acoustic" (a) and "Optical" (b) States of Primary Effectons

The "acoustic" a-state of the effectons is such a dynamic state when molecules or other particles composing the effectons, oscillate in the same phase (i.e. without changing the distance between them). The "optic" b-state of the effectons is such dynamic state when particles oscillate in the counterphase manner (i.e. with periodical change of the distance between particles). This state of primary effectons has a common features with Frölich's mode.

It is assumed in our model, that kinetic energies of "acoustic" (a) and "optical" (b) modes are equal $[T^a_{\rm kin} = T^b_{\rm kin}]$ in contrast to potential energies $[V^a < V^b]$. It means that the most probable impulses in (a) and (b) states and, consequently, the wave B length and **spatial dimensions of the effectons in the both states are equal** $([\lambda_{1,2,3}]^a = [\lambda_{1,2,3}]^b)$**.** The energy of intermolecular interaction (Van der Waals, Coulomb, hydrogen bonds etc.) in a-state are bigger than that in b-state. Consequently, the molecular polarizability in a-state also is bigger than in b-state. It means that dielectric properties of matter may change as a result of shift of the $(a \Leftrightarrow b)^{1,2,3}_{tr,lb}$ equilibrium of the effectons.

Primary Transitons (tr and lb)

Primary *transitons* represent intermediate transition states between (a) and (b) modes of primary effectons - translational and librational. Primary transitons (tr and lb) - are radiating or absorbing IR photons corresponding to translational and librational bands in oscillatory spectra. Such quantum transitions are not accompanied by the fluctuation of density but with the change of polarizability and dipole moment of molecules only. The volumes of primary transitons and primary effectons coincides (see Table 1).

Primary Electromagnetic and Primary Acoustic Deformons (tr, lb)

Electromagnetic primary deformons are a new type of quasiparticles (excitations) representing a $3D$ superposition of three standing electromagnetic waves. The IR photons (tr, lb) are radiated and absorbed as a result of $(a \Leftrightarrow b)^{1,2,3}_{tr,lb}$ transitions of primary effectons, i.e. corresponding primary transitons. Electromagnetic deformons appear as a result of superposition of 3 standing IR photons, penetrating in matter in different selected directions (1,2,3). We assume, that each of 3 pairs of counter-phase photons form a standing wave in the volume of condensed matter.

The linear dimension of each of three edges of primary deformon is determined by the wave length of three standing IR photons, superposing in the same space volume:

$$\lambda^{1,2,3} = [(n\tilde{\nu})^{-1}]^{1,2,3}_{tr,lb} \tag{2.5}$$

where: n is the refraction index and $(\tilde{\nu})_{tr,lb}$ - the wave number of translational or librational band. These quasiparticles as the biggest ones, are responsible for the long-range (distant) space-time correlation in liquids and solids.

In the case when $(b \rightarrow a)_{tr,lb}$ transitions of primary effectons are accompanied by big fluctuation of density (like cavitational fluctuation in liquid or defect formation in solid), they may be followed by emission of phonons instead of photons. It happens, when primary effectons are involved in the volume of macro- and supereffectons (see below). Primary *acoustic* deformons may originate or annihilate in such a way. However, the probability of collective spontaneous emission of photons during $(b \rightarrow a)_{tr,lb}$ transition of primary effectons is much higher than that of phonons, related to similar transition of macroeffectons (see below), as it leads from our theory.

The coherent electromagnetic radiation as a result of self- correlation of many dipole moments in composition of coherent cluster, like primary effectons, containing $\mathbf{N} \gg 1$ molecules is already known as **superradiance** (Dicke, 1954). *The time of collective transition in the case of superradiance is less than that of isolated molecule and intensity of superradiance* ($\mathbf{I} \sim \mathbf{N} \cdot \mathbf{h}\nu/\tau \sim \mathbf{N}^2$) *is much bigger than that from the same number of independent molecules* ($\mathbf{I} \sim \mathbf{N} \cdot \mathbf{h}\nu/\mathbf{T}_1 \sim \mathbf{N}$). The $(b \rightarrow a)$ transition time of the primary effectons has the reverse dependence on the $\mathbf{N}$ ($\tau \sim \mathbf{1}/\mathbf{N}$)**.** The relaxation time for isolated atoms or molecules ($\mathbf{T_1}$) is independent on $\mathbf{N}$. The main energy is radiated in the direction of most elongated volume, i.e. ends of tubes.

Secondary effectons (tr and lb)

In contrast to primary effectons, this type of quasiparticles is *conventional*. They are the result of averaging of the frequencies and energies of the "acoustic" (a) and "optical" (b) states of effectons with packing numbers $n_P > 0$, having the resulting impulse more than zero. For averaging the energies of such states the Bose-Einstein distribution was used under the condition when $T < T_0$ (T_0 is temperature of degeneration and, simultaneously, temperature of first order phase transition). Under this condition the chemical potential: $\mu = 0$ and distribution has a form of Plank equation.

Secondary effectons (tr and lb)

In contrast to primary effectons, the "acoustic" ($\overline{a}$) and "optical" ($\overline{b}$) states of secondary (mean) effectons are the result of averaging the energies of the effectons with packing numbers $n_P > 0$, having the resulting impulse different from zero. For this averaging the Bose-Einstein distribution was used under the condition: $T < T_0$ (T_0 is temperature of degeneration for **mesoscopic** Bose condensation (BC), equal to temperature of first order phase transition). Under this condition it is assumed, that the chemical potential: $\mu \simeq 0$ and Bose-Einstein distribution has a form of Plank equation [4].

Secondary transitons (tr and lb)

Secondary transitons, like primary ones are intermediate transition state between ($\overline{a}$) and ($\overline{\overline{b}}$) states of secondary effecton - translational and librational. As well as secondary effectons, these quasiparticles are conditional, i.e. a result of averaging. It is assumed that the volumes of secondary transitons and secondary effectons coincide. The $(\bar{a} \Leftrightarrow \bar{b})_{tr,lb}$ transition states of secondary effectons, in contrast to that of primary effectons, are accompanied by the fluctuation of density. Secondary transitons are responsible for radiation and absorption of phonons.

Secondary "acoustic" deformons (tr and lb)

This type of quasiparticles is also conditional as a result of 3D superposition of averaged thermal phonons. These conventional phonons originate and annihilate in a process of $(\bar{a} \Leftrightarrow \bar{b})_{1,2,3}$ thermoactivated transitions of secondary conventional effectons. These states correspond to translational and librational transitons.

Convertons (tr $\Leftrightarrow$ lb)

These important excitations are introduced in our model as a reversible transitions between translational and librational primary effectons. The *(acon) convertons* correspond to transitions between the ($a_{tr} \rightleftharpoons a_{lb}$) states of these effectons and *(bcon) convertons* - to that between their ($b_{tr} \rightleftharpoons b_{lb}$) states. As

far as the dimensions of translational primary effectons are much less than librational ones, the *convertons* could be considered as [dissociation $\rightleftharpoons$ association] of the primary librational effectons (coherent clusters). Both of convertons, (*acon*) and (*bcon*), are accompanied by density fluctuation, inducing phonons with corresponding frequency in the surrounding medium. All kinds of Convertons may be termed 'flickering' clusters.

The ca- and cb- deformons, induced by convertons

Three-dimensional (3D) superposition of phonons, irradiated by two types of convertons, *acon* and *bcon*, represents in our model the acoustic *ca- and cb-deformons.* They have properties similar to that of *secondary deformons,* discussed above.

The c-Macrotransitons (Macroconvertons) and c-Macrodeformons

Simultaneous excitation of the *acon* and *bcon* types of convertons in the volume of primary librational effectons leads to origination of big fluctuations, like cavitational ones, termed *c-Macrotransitons or Macroconvertons.* In turn, corresponding density fluctuations induce in surrounding medium high frequency thermal phonons. The 3D-superposition these standing phonons forms *c- Macrodeformons.*

Macroeffectons (tr and lb)

Macroeffectons (A and B) are collective *simultaneous* excitations of the primary and secondary effectons in the $[A \sim (a,\, \bar{a})]_{tr,lb}$ and $[B \sim (b,\, \bar{b})]_{tr,lb}$ states in the volume of primary electromagnetic translational and librational deformons, respectively. This correlation of primary and secondary states results in significant deviations from thermal equilibrium. The A and B states of macroeffectons (tr and lb) may be considered as the most probable volume-orchestrated (correlated) thermal fluctuations of condensed matter.

Macrodeformons or Macrotransitons (tr and lb)

This type of conventional quasiparticles is considered in our model as an *intermediate* transition state of macroeffectons. The $(A \rightarrow B)_{tr,lb}$ and $(B \rightarrow A)_{tr,lb}$ transitions are represented by the coherent transitions of primary and secondary effectons *in the volume of primary electromagnetic deformons* - translational and librational. The $(A \rightarrow B)_{tr,lb}$ transition of macroeffecton is accompanied by simultaneous absorption of 3 pairs of photons and that of phonons in the form of electromagnetic deformons. If $(B \rightarrow A)_{tr,lb}$ transition occurs without emission of photons, then all the energy of the excited B-state is transmitted to the energy of fluctuation of density and entropy of Macroeffecton as an isolated mesosystem. It is a dissipative process: transition from the more ordered structure of matter to the less one, termed Macrodeformons. The big fluctuations of density during $(A \Leftrightarrow B)_{tr,lb}$ transitions of macroeffectons, i.e. macrodeformons are responsible for the Rayleigh central component in Brillouin spectra of light

scattering [15]. Translational and librational macrodeformons are also related to the corresponding types of viscosity and self-diffusion [16]. The volumes of macrotransitons, equal to that of macrodeformons (tr or lb) and macroeffectons, coincide with that of **tr** or **lb primary electromagnetic deformons,** correspondingly.

Supereffectons

This mixed type of conventional quasiparticles is composed of translational and librational macroeffectons correlated in space and time in the volumes of superimposed electromagnetic primary deformons (translational and librational - simultaneously). Like macroeffectons, supereffectons may exist in the ground (A_S^*) and excited (B_S^*) states representing strong deviations from thermal equilibrium state.

Superdeformons or Supertransitons

This collective excitations have the lowest probability as compared to other quasiparticles of our model. Like macrodeformons, superdeformons represent the intermediate ($A_S^* \Leftrightarrow B_S^*$) transition state of supereffectons. In the course of these transitions the translational and librational macroeffectons undergo simultaneous

$$[(A \Leftrightarrow B)_{tr} \;\; and \;\; (A \Leftrightarrow B)_{lb}] \quad \text{transitions}$$

The ($A_S^* \rightarrow B_S^*$) transition of supereffecton may be accompanied by the absorption of two electromagnetic deformons - translational and librational simultaneously. The reverse ($B_S^* \rightarrow A_S^*$) relaxation may occur without photon radiation. In this case the big **cavitational fluctuation** originates. Such a process plays an important role in the processes of sublimation, evaporation and boiling.

The equilibrium dissociation constant of the reaction:

$$H_2O \rightleftharpoons H^+ + HO^- \tag{2.6}$$

should be related with equilibrium constant of supertransitons: $K_{B_S^* \rightleftharpoons A_S^*}$. The $A_S^* \rightarrow B_S^*$ cavitational fluctuation of supereffectons can be accompanied by the activation of reversible dissociation of small fraction of water molecules.

In contrast to primary and secondary transitons and deformons, the notions of [macro- and supertransitons] and [macro- and superdeformons] coincide. Such types of *transitons and deformons* represent the dynamic processes in the same volumes of corresponding primary electromagnetic deformons.

Considering the transitions of all types of *translational* deformons (primary, secondary and macrodeformons), one must keep in mind that the *librational* type of modes remains the same. And vice versa, in case of librational deformons, translational modes remain unchanged. Only the realization of a *convertons and supereffectons are accompanied by the interconversions between the translational and librational modes, between translational and librational effectons.*

Interrelation Between Quasiparticles Forming Solids and Liquids

Our model includes **24** types of quasiparticles (Table. 1):

$$\left[\begin{array}{c} 4 \text{ - } \textit{Effectons} \\ 4 \text{ - } \textit{Transitons} \\ 4 \text{ - } \textit{Deformons} \end{array}\right] \quad \begin{array}{l} \text{translational and librational, including} \\ \text{primary and secondary} \end{array} \qquad \text{(I)}$$

$$\left[\begin{array}{c} 2 \text{ - } \textit{Convertons} \\ 2 - C\textit{-deformons} \\ 1 - Mc\textit{-transiton} \\ 1 - Mc\textit{-deformon} \end{array}\right] \quad \begin{array}{l} \text{the set of interconvertions} \\ \text{between translational and librational} \\ \text{primary effectons} \end{array} \qquad \text{(II)}$$

$$\left[\begin{array}{c} 2 \text{ - } \textit{Macroeffectons} \\ 2 \text{ - } \textit{Macrodeformons} \end{array}\right] \quad \begin{array}{l} \text{translational and librational} \\ \text{(spatially separated)} \end{array} \qquad \text{(III)}$$

$$\left[\begin{array}{c} 1 \text{ - } \textit{Supereffectons} \\ 1 \text{ - } \textit{Superdeformons} \end{array}\right] \quad \begin{array}{l} \text{translational } \rightleftharpoons \text{ librational} \\ \text{(superposition of } tr \text{ and } lb \text{ effectons} \\ \text{and deformons in the same volume)} \end{array} \qquad \text{(IV)}$$

Each next level in the hierarchy of quasiparticles (I - IV) introduced in our model, is based on unification of the properties of the previous ones. All of these quasiparticles are constructed on the same physical principles. Part of them is a result of 3D - superposition of different types of standing waves: de Broglie waves, IR electromagnetic photons and phonons.

Such a system in equilibrium state can be handled as a gas of quasiparticles. As far each of the effecton's types: $[tr]$ and $[lb]$, macroeffectons $[tr + lb]$ and supereffectons $[tr/lb]$ have two states (acoustic and optic) the total number of excitations, as one can calculate from the table above, is equal to:

$$\mathbf{N}_{ex} = \mathbf{31}$$

This classification reflects the *duality of matter and field* and represent their self-organization and interplay on mesoscopic and macroscopic levels.

Our hierarchical system includes a gradual transition from the *Order* (primary effectons, transitons and deformons) to *Disorder* (macro- and superdeformons). It is important, however, that in accordance with the model proposed, this thermal *Disorder is "organized"* by hierarchical superposition of definite types of the ordered quantum excitations. It means that the final dynamics condensed matter only "looks" as chaotic one. Our approach makes it possible to take into account the Hidden Order of Condensed Matter in form mesoscopic Bose condensate and its dynamics for better understanding of Disorder.

The long-distance correlation between quasiparticles is determined mainly by the biggest ones - an *electromagnetic primary deformons*, involving in its volume a huge number of primary and secondary effectons. The volume of primary deformons [tr and lb] could be subdivided on two equal parts, within

the nodes of 3D standing IR electromagnetic waves. The big number of the effectons in each of these parts is equal also. The dynamics effectons is correlated in such a way, that when one half of their quantity in the volume of big primary deformon undergo $(a \to b)_{tr,lb}$ transitions, the other half of the effectons undergo the opposite $(b \to a)_{tr,lb}$ transition. These processes may compensate each other due to exchange of IR photons and phonons in equilibrium conditions.

The increasing or decreasing in the concentration of primary deformons is directly related to the shift of $(a \Leftrightarrow b)_{tr,lb}$ equilibrium of the primary effectons leftward or rightward, respectively. This shift, in turn, leads also to corresponding changes in the energies and concentrations of secondary effectons, deformons and, consequently, to that of super- and macro-deformons. **It means the existing of feedback reaction between subsystems of the effectons and deformons, necessary for long-range self-organization in macroscopic volumes of condensed matter.**

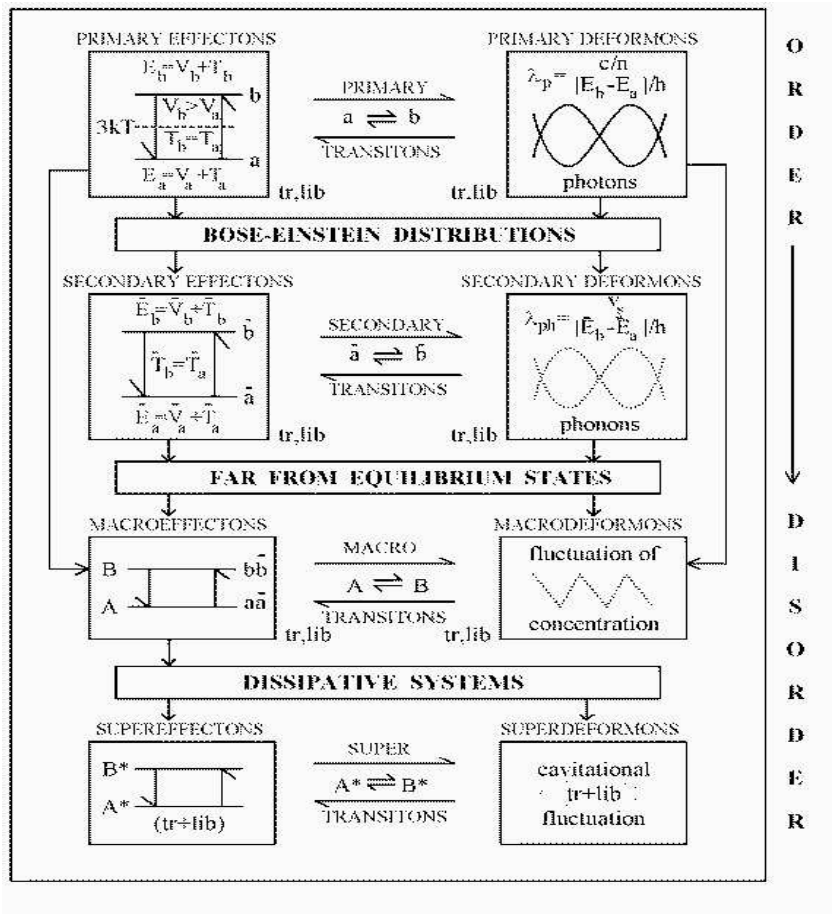

Table 1. Schematic representation of the 18 types of quasiparticles of condensed matter as a hierarchical dynamic system, based on the effectons, transitons and deformons. Total number of *quasiparticles*, introduced in Hierarchic concept is 24. Six collective excitations, related to *convertons*- interconversions between primary

librational and translational effectons and their derivatives are not represented here for the end of simplicity.

The situation is possible when spontaneous oscillations between the subsystems of effectons and deformons are not accompanied by the change in the total internal energy due to *compensation effect*. In such a way a long-period macroscopic oscillations in liquids, revealed experimentally (Chernicov, 1990a, 1990b), could be explained. **Such kind of phenomena, related to equilibrium shift of two subsystems, could be responsible for long relaxation (memory) of water containing systems after different perturbations (like magnetic treatment, ultra high dilution, etc.)**. The instability of macrosystem arises from *competition between discrete quantum* and *averaged thermal equilibrium types of energy distributions* of coherent molecular clusters, as it leads from our theoretical calculations.

The total internal energy of substance is determined by the contributions of all types of quasiparticles with due regard for their own energy, concentration and probability of excitation. It leads from our simulations, that contributions of *super*- and *macro*effectons and corresponding *super*- and *macro*deformons as well as *polyeffectons and coherent superclusters* to the internal energy of matter normally are small, due to their low probability of excitation, big volume and, consequently, low concentration.

Polyeffectons and superclusters are the result of primary effectons assembly (one-dimensional, two- or three-dimensional), stabilized by Josephson's junctions.

The sizes of primary effectons (translational and librational) determine the mesoscopic scale of the condensed matter organization. Domains, nods, crystallites, observed in solid bodies, liquid crystals, polymers and biopolymers are the consequence of primary effectons and their association.

3. THE MAIN STATEMENTS AND BASIC FORMULAE OF HIERARCHIC MODEL

As far the acoustic (a) and optical (b) thermal coherent modes of molecules in composition of elementary cells or bigger clusters of the condensed matter are anharmonic, the quantum $a \Leftrightarrow b$ transitions (beats) with absorption and radiation of phonons or photons can exist.

The number of acoustic and optical modes is the same and equal to three (Kaivarainen, 1995), if oscillation of all p-atoms in the basis are coherent in both optical and acoustic dynamic states. Remnant modes are degenerated.

The states of system, minimizing the uncertainty relation, when:

$$[\Delta p \cdot \Delta x \sim \hbar \ \ and \ \ \Delta x = L \sim \hbar/\Delta p]_{1,2,3} \tag{3.1}$$

are quantum *coherent states*.

A system of the effectons could be considered as a partially degenerate Bose-gas. The degree of the degenerateness is proportional to the number of molecules in the volume of primary effectons. Degeneration in liquids grows up at lowering temperature and make a jump up as a result of (liquid → solid) phase transition as it leads from our theory and computer calculations.

It is known from the Bose-Einstein theory of condensation, developed by London (1938), that if the **degeneration factor:**

$$\lambda = \exp(\mu/kT) \tag{3.2}$$

is close to $\lambda \simeq 1$ at a low chemical potential value:

$$\mu \ll kT \tag{3.2a}$$

then the *contribution of bosons with the resulting impulse* $P_{ef} \simeq 0$ (like primary effectons) cannot be neglected, when calculating internal energy.

We assume in our theory that for all types of primary and secondary effectons of condensed matter (solids and liquids), the condition (3.2a) is valid.

Partial Bose-Einstein condensation leads to the coherence of the waves B of molecules and atoms forming primary effectons in the both: acoustic (a) and optic (b) states. Primary effectons are described with wave functions coherent in the volume of an effecton.

In non ideal Bose-gas, despite the partial Bose-condensation, the quasiparticles exist with nonzero impulse, termed as *secondary* effectons. These effectons obeys the Bose-Einstein statistics.

The sizes of primary effectons determine the mesoscopic scale of the condensed matter organization. **According to our model, the domains, nods, crystallites, and clusters observed in solid bodies and in liquid crystals, polymers and biopolymers - can be a consequence of primary translational or librational effectons.**

Stabilization of molecules, atoms or ions in composition of coherent clusters (effectons) and correlation between different effectons could be provided by distant Van der Waals interaction and new *Resonant Vibro-Gravitational Interaction,* introduced in our theory (see Section 10.4).

It leads from *quantitative consequences* of mesoscopic concept, that [gas → liquid] phase transition is related with appearance the conditions for partial Bose-condensation, when the primary librational effectons, containing more than one molecule emerge (Kaivarainen, 1995, 1996). At the same time it means the beginning of degeneration when the chemical potential $\mu \to 0$. At this condition wave B length, corresponding to librations, starts to exceed the mean distances between molecules in the liquid phase.

It means that the temperature, at which the phase transition [*gas → liquid*] occurs, coincides with the temperature of partial Bose- condensation (T_c), [i.e. primary librational effectons formation] and degeneration temperature (T_0).

The changes of **quasiparticles volume and shape** in three dimensional (3D) space are related to corresponding changes in the impulse space.

The total macroscopic Bose-condensation, in accordance with our model, responds to conditions, when [$a \Leftrightarrow b$] equilibrium of primary effectons strongly shifts to the main (a)- state and (b)- state becomes thermally inaccessible.

At the same time the wave B length tends to macroscopic value. For quantum systems at temperature (T) higher than degeneration temperature T_0 $(T > T_0)$, when chemical potential $(\mu_i = \partial G_i/\partial n_i) < 0$ has a negative value, the mean number of Bose-particles (n_i) in state (i) is determined by the Bose- Einstein distribution:

$$\overline{n}_i = \{\exp[(\epsilon_i - \mu_i)/kT] - 1\}^{-1} \tag{3.3}$$

where ϵ_i is the energy of the particle in state (i). For "normal" condensed matter $\epsilon_i \gg \mu \ll kT$.

The Bose-Einstein statistics, in contrast to the Maxwell- Boltzmann statistics, is applied to the indistinguishable Bose- particles with zero or integer spin values. The Fermi-Dirac distribution is valid for systems of indistinguishable particles with a semi-integer spin obeying the Pauli principle.

In the case of condensed matter at the temperature:

$$0 < T < [T_0 \cong T_c]$$

N* particles of Bose condensate have a zero impulse (Ashkroft, Mermin, 1976):

$$N^* \simeq N[1 - (T/T_0)^{3/2}] \tag{3.4}$$

where N is the total number of particles in a system.

3.1. Parameters of individual de Broglie waves (waves B)

The known de Broglie relation expressing Wave-Particle Duality, has a simple form:

$$\overrightarrow{p} = \hbar \overrightarrow{k} = h/\overrightarrow{\lambda}_B$$
$$\overrightarrow{p} = \hbar/\overrightarrow{L}_B = m\overrightarrow{v}_{gr}$$

where $\vec{k} = 2\pi/\vec{\lambda} = 1/\vec{L}_B$ is the wave number of wave B with length $\vec{\lambda} = 2\pi\vec{L}_B$, $\vec{p}$ is the impulse (momentum) of particle with mass (m) and group velocity (v_{gr}), $\hbar = h/2\pi$ is the Plank constant.

Each particle can be represented as wave packet with group velocity:

$$v_{gr} = \left(\frac{d\omega_b}{dk}\right)_0$$

and phase velocity:

$$v_{ph} = \frac{\omega_b}{k} \tag{3.4a}$$

where: ω_B is the angle frequency of wave B determining the total energy of the wave $B : (E_B = \hbar\omega_B)$.

Total energy is equal to the sum of kinetic (T_k) and potential (V_B) energies and is related to particle's mass and product of phase and group velocities ($v_{gr}v_{ph}$) as follows (Grawford, 1973):

$$E_B = \hbar\omega_B = T_k + V_B = \frac{(\hbar k)2}{2m} + V_B = mv_{gr}v_{ph} \tag{3.4b}$$

where (m) is particle mass; (c) is light velocity.

From 3.4a and 3.4b it is possible to get an important relation between phase and group velocities of wave B and its kinetic, potential and total energy:

$$\frac{v_{ph}}{v_{gr}} = \frac{T_k + V_B}{2T_k} = \frac{E_B}{2T_k} \tag{3.4c}$$

3.2. Parameters of de Broglie waves of molecules in composition of condensed matter

The formulae given below allow to calculate the frequencies of the corresponding primary waves B in the directions 1,2,3 in a and b states of primary effectons (translational and librational) (Kaivarainen, 1989, 1995, 1996):

$$\left[\nu^a_{1,2,3}\right]_{tr,lb} = \left[\frac{\nu_p^{1,2,3}}{\exp(h\nu_p^{1,2,3}/kT) - 1}\right]_{tr,lb} \tag{3.5}$$

$$\left[\nu^b_{1,2,3}\right]_{tr,lb} = \left[\nu^a_{1,2,3} + \nu_p^{1,2,3}\right]_{tr,lb} \tag{3.6}$$

The most probable frequencies of photons $\left[\nu_p^{1,2,3}\right]_{tr,lb}$ are related to the wave numbers of the maxima of corresponding bands (tr and lib) $\left[\tilde{\nu}_p^{1,2,3}\right]_{tr,lb}$ in oscillatory spectra:

$$\left[\nu_p^{1,2,3}\right]_{tr,lb} = c\left[\tilde{\nu}_p^{1,2,3}\right]_{tr,lb} \tag{3.7}$$

where (c) is light velocity. For water the most probable frequencies of photons, corresponding to $(a \Leftrightarrow b)_{tr}$ transitions of primary translational effectons are determined by maxima with the wave numbers: $\widetilde{\nu}_p^{(1)} = 60cm^{-1}$; $\widetilde{\nu}_p^{(2)} = \widetilde{\nu}_p^{(3)} = 190cm^{-1}$.

The band $\tilde{\nu}_p^{(1)} = \tilde{\nu}_p^{(2)} = \tilde{\nu}_p^{(3)} = 700cm^{-1}$ corresponds to the $(a \Leftrightarrow b)_{lb}$ transitions of primary librational effectons. The degenerateness of frequencies characterizes the isotropy of the given mobility type for molecules.

The distribution (3.5) coincides with the Plank formula, for the case when frequency of a quantum oscillator is equal to the frequency of photon and:

$$\nu_p = \overline{n}_p\nu_p \tag{3.8}$$

where $\bar{n}_p = [\exp(h\nu_p/kT - 1)]^{-1}$ is the mean number of photons with the frequency ν_p..

The transition $a \to b$ means that $\bar{n}_p$ increases by one

$$\nu^b = \nu^a + \nu_p = \overline{n}\nu_p + \nu_p = \nu_p(\overline{n} + 1) \tag{3.9}$$

The derivation of the formula (3.5) is based upon the assumption that $(a \Leftrightarrow b)_{1,2,3}$ transitions are analogous to the beats in a system of two weakly interacting quantum oscillators.

In such a case the frequency $(\nu_p^{1,2,3})$ of photons is equal to the difference between the frequencies of waves B forming a primary effectons in (b) and (a) states as a frequency of quantum beats (Grawford, 1973):

$$\left[\nu_p^{1,2,3} = \nu_{1,2,3}^b - \nu_{1,2,3}^a = \Delta\nu_B^{1,2,3}\right]_{tr,lb} \tag{3.10}$$

where $\Delta\nu_B^{1,2,3}$ is the most probable difference between frequencies of waves B in the marked directions (1,2,3).

The ratio of concentrations for waves B in a and b states (n_B^a/n_B^b) at such consideration is equal to the ratio of wave B periods $T^{a,b}$ or the inverse ratio of wave B frequencies in these states:

$$(T^a/T^b)_{1,2,3} = (\nu^b/\nu^a)_{1,2,3}.$$

At the same time, the ratio of concentrations is determined with the Boltzmann distribution. So, the formula is true:

$$\left(\frac{n_B^a}{n_B^b}\right)_{1,2,3} = \left(\frac{\nu^b}{\nu^a}\right)_{1,2,3} = \exp\left(\frac{h\nu_B^{1,2,3}}{kT}\right) = \exp\left(\frac{h\nu_p^{1,2,3}}{kT}\right) \tag{3.11}$$

Substituting the eq.(3.10) into (3.11) we derive the eq.(3.5), allowing to find $(\nu_{1,2,3}^a)_{tr,lb}$ and $(\nu_{1,2,3}^b)_{tr,lb}$ from the data of oscillation spectroscopy at every temperature.

The energies of the corresponding three waves B ($E_{1,2,3}^a$ and $E_{1,2,3}^b$) and that of the primary effectons as 3D standing waves with energies (E_{ef}^a and E_{ef}^b) in a and b states are equal to:

$$\left[E_{1,2,3}^a = h\nu_{1,2,3}^a\right]_{tr,lb}; \quad \left[E_{ef}^a = h(\nu_1^a + \nu_2^a + \nu_3^a\right]_{tr,lb} \tag{3.12}$$

$$\left[\ E_{1,2,3}^b = h\nu_{1,2,3}^b\ \right]_{tr,lb}; \quad \left[E_{ef}^b = h(\nu_1^b + \nu_2^b + \nu_3^b\right]_{tr,lb} \tag{3.13}$$

In our model energies of quasiparticles in each state are thus determined only by the three selected coherent modes in directions (1,2,3). All remnant degrees of freedom: $(3n - 3)$, where n is the number of molecules forming effectons or deformons, are degenerated due to their coherence.

The mean packing numbers for $\bar{a}$ and $\bar{b}$ states are thereby expressed with the formula (1.27), and the mean energies ($\bar{E}^a_{1,2,3} = h\bar{\nu}^a_{1,2,3}$ and $\bar{E}^b_{1,2,3} = h\bar{\nu}^b_{1,2,3}$) - with Bose-Einstein distribution (1.21; 1.28), coincident with the Plank formula at chemical potential $\mu = 0$.

Finally, the averaged Hamiltonians of (a, $\bar{a}$) and (b, $\bar{b}$) states of the system containing primary and secondary effectons (translational and librational) have such a form:

$$\left[\ \bar{H}^a_{1,2,3} = E^a_{1,2,3} + \bar{E}^a_{1,2,3} = h\nu^a_{1,2,3} + h\bar{\nu}^a_{1,2,3}\ \right]_{tr,lb} \tag{3.14}$$

$$\left[\ \bar{H}^b_{1,2,3} = E^b_{1,2,3} + \bar{E}^b_{1,2,3} = h\nu^b_{1,2,3} + h\bar{\nu}^b_{1,2,3}\ \right]_{tr,lb} \tag{3.15}$$

where

$$\left[\bar{\nu}^a_{1,2,3} = \frac{\nu^a_{1,2,3}}{\left[\ \exp(h\nu^a_{1,2,3})/kT - 1\ \right]} = \frac{\bar{v}^a_{ph}}{\bar{\lambda}^{1,2,3}_a}\right]_{tr,lb} \tag{3.16}$$

$$\left[\bar{\nu}^b_{1,2,3} = \frac{\nu^b_{1,2,3}}{\left[\ \exp(h\nu^b_{1,2,3})/kT - 1\ \right]} = \frac{\bar{v}^b_{ph}}{\bar{\lambda}^{1,2,3}_b}\right]_{tr,lb} \tag{3.17}$$

$\bar{\nu}^a_{1,2,3}$ and $\bar{\nu}^b_{1,2,3}$ are the mean frequency values of each of three types of coherent waves B forming effectons in ($\bar{a}$) and ($\bar{b}$) states; $\bar{v}^a_{ph}$ and $\bar{v}^b_{ph}$ are the corresponding phase velocities.

The resulting Hamiltonian for *photons,* which *form the primary deformons* and *phonons* forming *secondary deformons*, are determined with the term-wise subtraction of the formula (3.14) from the formula (3.15):

$$\mid \Delta\bar{H}_{1,2,3} \mid_{tr,lb} = h \mid \nu^b_{1,2,3} - \nu^a_{1,2,3} \mid_{tr,lb} + h \mid \bar{\nu}^b_{1,2,3} - \bar{\nu}^a_{1,2,3} \mid_{tr,lb} =$$

$$= h(\nu^{1,2,3}_p)_{tr,lb} + h(\nu^{1,2,3}_{ph})_{tr,lb} \tag{3.18}$$

where the frequencies of six IR photons, propagating in directions $(\pm 1, \pm 2, \pm 3)$ and composing the primary deformons in the interceptions are equal to:

$$(\nu^{1,2,3}_p)_{tr,lb} = \mid \nu^b_{1,2,3} - \nu^a_{1,2,3} \mid_{tr,lb} = (c/\lambda^{1,2,3}_p \cdot n)_{tr,lb} \tag{3.19}$$

where: [c] and [n] are the light velocity and refraction index of matter; $\lambda^{1,2,3}_{ph}$ are the wavelengths of photons in directions (1,2,3); and:

$$(\nu^{1,2,3}_{ph})_{tr,lb} = \mid \overline{\nu}^b_{1,2,3} - \overline{\nu}^a_{1,2,3} \mid_{tr,lb} = (v_s/\lambda^{1,2,3}_{ph})_{tr,lb} \tag{3.20}$$

are the frequencies of six phonons (translational and librational) in the directions

$(\pm 1, \pm 2, \pm 3)$, forming secondary acoustic deformons; v_s is the sound speed; $\bar{\lambda}_{ph}^{1,2,3}$ are the wavelengths of phonons in three selected directions.

The corresponding energies of photons and phonons are:

$$E_p^{1,2,3} = h\nu_p^{1,2,3}; \quad E_{ph}^{1,2,3} = h\bar{\nu}_{ph}^{1,2,3} \tag{3.21}$$

The formulae for the wave B lengths of primary and secondary effectons are derived from (3.5) and (3.16):

$$\begin{array}{l} \lambda_a^{1,2,3})_{tr,lb} = \lambda_b^{1,2,3} = v_p^a/\nu_{1,2,3}^a = \\ = (v_p^a/\nu_p^{1,2,3}) \left[\ \exp(h\nu_p^{1,2,3})/kT - 1 \ \right]_{tr,lb} \end{array} \tag{3.22}$$

$$\begin{array}{l} \bar{\lambda}_a^{1,2,3})_{tr,lb} = \bar{\lambda}_b^{1,2,3} = \bar{v}_{ph}^a/\bar{\nu}_{1,2,3}^a = \\ = (\bar{v}_{ph}^a/\bar{\nu}_{ph}^{1,2,3}) \left[\ \exp(h\bar{\nu}_{ph}^{1,2,3})/kT - 1 \ \right]_{tr,lb} \end{array} \tag{3.23}$$

The wavelengths of photons and phonons forming the *primary* and *secondary deformons* can be determined as follows

$$(\lambda_p^{1,2,3})_{tr,lb} = (c/n\nu_p^{1,2,3})_{tr,lb} = 1/(\widetilde{\nu})_{tr,lb}^{1,2,3}$$

where: $(\tilde{\nu})_{tr,lb}^{1,2,3}$ are wave numbers of corresponding bands in the oscillatory spectra of condensed matter.

$$(\bar{\lambda}_{ph}^{1,2,3})_{tr,lb} = (\bar{v}_s/\bar{\nu}_{ph}^{1,2,3})_{tr,lb}$$

For calculations according to the formulae (2.59) and (2.60) it is necessary to find a way to calculate the resulting phase velocities of waves B forming primary and secondary effectons (v_{ph}^a and $\bar{v}_{ph}^a$).

3.3. Phase velocities of standing de Broglie waves, forming new types of quasiparticles

In crystals three phonons with different phase velocities can propagate in *the* direction set by the longitudinal wave normal. In a general case, two quasi-transversal waves "fast" ($v_\perp^f$) and "slow" ($v_\perp^s$) and one quasi-longitudinal ($v_\parallel$) wave propagate (Ashkroft and Mermin, 1976).

The propagation of **transversal** acoustic waves is known to be accompanied by smaller deformations of the lattice than that of **longitudinal** waves, when they are caused by *external* impulses. The thermal phonons, spontaneously originating and annihilating under conditions of heat equilibrium may be accompanied by even smaller perturbations of the structure and could be considered as **transversal** phonons.

Therefore, we assume, that in the absence of external impulses in solid state: $v_\perp^f \approx v_\perp^s = v_{ph}^{1,2,3}$ and the *resulting thermal phonons* velocity is determined as:

$$v_s^{\text{res}} = (v_\perp^{(1)} v_\perp^{(2)} v_\perp^{(3)})^{1/3} = v_{ph} \tag{3.24}$$

In liquids the resulting sound speed has an isotropic value:

$$v_s^{\rm liq} = v_{ph}.$$

According to our model, the resulting velocity of elastic waves in condensed media is related to the phase velocities of primary and secondary effectons in both (acoustic and optic) states and that of deformons (translational and librational) in the following way:

$$\left[\ v_s = f_a v_{ph}^a + f_b v_{ph}^b + f_d v_{ph}^d\ \right]_{tr,lb} \tag{3.25}$$

$$\left[\ \bar{v}_s = \bar{f}_a \bar{v}_{ph}^a + \bar{f}_b \bar{v}_{ph}^b + \bar{f}_d \bar{v}_{ph}^d\ \right]_{tr,lb} \tag{3.26}$$

where: v_{ph}^a, v_{ph}^b, $\bar{v}_{ph,}^a$ $\bar{v}_{ph}^b$ are phase velocities of the most probable and mean effectons in the "acoustic" and "optic" states; and

$$v_{ph}^d = v_{ph}^d = v_s$$

are phase velocities of primary and secondary acoustic deformons, equal to phonons velocity.

Nevertheless, $(a \to b)_{tr,lb}$ or $(b \to a)_{tr,lb}$ transitions of primary effectons are mainly related with absorption or emission of photons, the rate of such process (relaxation time) is limited by the rate of changing the mode of oscillations in (a) and (b) state, i.e. by sound velocity $(v_s = v_{ph})$. The phonons [absorption/radiation] during these transitions could accompanied the like processes in composition of macrodeformons;

$$f_a = \frac{P_a}{P_a + P_b + P_d};\ \ f_b = \frac{P_b}{P_a + P_b + P_d};\ \ f_d = \frac{P_d}{P_a + P_b + P_d} \tag{3.27}$$

and

$$\overline{\bar{f}_a} = \frac{\bar{P}_a}{\bar{P}_a + \bar{P}_b + \bar{P}_d};\ \ \overline{f_b} = \frac{\bar{P}_b}{\bar{P}_a + \bar{P}_b + \bar{P}_d};\ \ \overline{f_d} = \frac{\bar{P}_d}{\bar{P}_a + \bar{P}_b + \bar{P}_d} \tag{3.28}$$

are the probabilities of corresponding states of the primary (f) and secondary quasiparticles; P_a, P_b, P_d and $\bar{P}_a$, $\bar{P}_{b,}$ $\bar{P}_d$ - relative probabilities of excitation (thermoaccessibilities) of the primary and secondary effectons and deformons (see eqs. 4.10, 4.11, 4.18, 4.19, 4.25 and 4.26).

Using eq. (3.4c) it is possible to express the phase velocities in b and $\bar{b}$ states of effectons (v_{ph}^b and $\bar{v}_{ph}^b$) via (v_{ph}^a and $\bar{v}_{ph}^a$) in the following way:

$$\left[\frac{v_{ph}^b}{v_{gr}^b}\right]_{tr,lb} = \left[\frac{E_{\rm tot}^b}{2T_k^b}\right]_{tr,lb} = \left[\frac{h\nu_{\rm res}^b}{m(v_{gr}^b)^2}\right]_{tr,lb} \tag{3.29}$$

From this equation, we obtain for the *most probable* phase velocity in (b) state:

$$(v^b_{ph})_{tr,\mathrm{lib}} = \left[\lambda^{\mathrm{res}}_{ph}\nu^{\mathrm{res}}_b\right]_{tr,\mathrm{lib}} = \left[(v^a_{ph})\frac{\nu^{\mathrm{b}}_{res}}{\nu^{\mathrm{a}}_{res}}\right]_{tr,lb} \tag{3.30}$$

We keep in mind that according to our model $v^b_{gr} = v^a_{gr}$ and $\bar{v}^b_{gr} = \bar{v}^a_{gr}$, i.e. the group velocities of both states are equal.

Likewise for the *mean* phase velocity in $\bar{b}$-state of effectons we have:

$$(\bar{v}^b_{ph})_{tr,lb} = \left[\left(\ \bar{v}^a_{ph}\ \right)\frac{\bar{\nu}^{\mathrm{res}}_b}{\bar{\nu}^{\mathrm{res}}_a}\right]_{tr,lb} \tag{3.31}$$

where in (3.30):

$$\left[\begin{array}{l}\nu^b_{\mathrm{res}} = (\nu^b_1\nu^b_2\nu^b_3)^{1/3}\\ \nu^a_{\mathrm{res}} = (\nu^a_1\nu^a_2\nu^a_3)^{1/3}\end{array}\right]_{tr,lb} \tag{3.32}$$

are the resulting frequencies of the most probable (primary) effectons in b and a states. They can be calculated using the eqs. (3.5 and 3.6); frequencies; and in (3.31):

$$\left[\overline{\nu}^b_{\mathrm{res}} = (\overline{\nu}^b_1\overline{\nu}^b_2\overline{\nu}^b_3)^{1/3}\right]_{tr,lb} \tag{3.33}$$

$$\left[\overline{\nu}^a_{\mathrm{res}} = (\overline{\nu}^a_1\overline{\nu}^a_2\overline{\nu}^a_3)^{1/3}\right]_{tr,lb} \tag{3.34}$$

are the resulting frequencies of the mean effectons in $\bar{b}$ and $\bar{a}$ states. They can be estimated according to eqs. (3.17 and 3.16).

Using eqs. (3.25 and 3.30), we find the formulas for the *resulting phase velocities* of the primary translational and librational effectons in (a) state:

$$\left(v^a_{ph}\right)_{tr,lb} = \left[\frac{v_s\frac{(1-f_d)}{f_a}}{1+\frac{P_b}{P_a}\left(\frac{\nu^b_{\mathrm{res}}}{\nu^a_{\mathrm{res}}}\right)}\right]_{tr,lb} \tag{3.35}$$

Similarly, for the resulting phase velocity of secondary effectons in (a) state we get from (3.26) and (3.31):

$$\left(\bar{v}^a_{ph}\right)_{tr,lb} = \left[\frac{v_s\frac{(1-\bar{f}_d)}{\bar{f}_a}}{1+\frac{\bar{P}_b}{P_a}\left(\frac{\bar{\nu}^b_{\mathrm{res}}}{\bar{\nu}^a_{\mathrm{res}}}\right)}\right]_{tr,lb} \tag{3.36}$$

As will be shown below, it is necessary to know v^a_{ph} and $\bar{v}^a_{ph}$ to determine the *concentration* of the primary and secondary effectons. When the values of resulting phase velocities in a and $\bar{a}$ states of effectons are known, then from eqs. (3.30) and (3.31) it is easy to express resulting phase velocities in b and $\bar{b}$ states of translational and librational effectons.

3.4. Concentrations of quasiparticles, introduced in Hierarchic model of condensed matter

It has been shown by Rayleigh that the concentration of the standing waves of any type with wave lengths within the range: λ to $\lambda + d\lambda$ is equal to:

$$n_\lambda d\lambda = \frac{4\pi d\lambda}{\lambda^4} \tag{3.37}$$

or, expressing wave lengths via their frequencies and phase velocities $\lambda = v_{ph}/\nu$ we obtain:

$$n_\nu d\nu = 4\pi \frac{\nu^2 d\nu}{v_{ph}^2} \tag{3.38}$$

For calculation the concentration of standing waves within the frequency range from zero to the definite characteristic frequency, for example, to the most probable (ν_a) or mean ($\bar{\nu}_a$) frequency of wave B, then eq. (3.38) should be integrated:

$$n_a = \frac{4\pi}{v_{ph}^3} \int_0^{\nu_a} \nu^2 d\nu = \frac{4}{3}\pi \left(\frac{\nu^a}{v_{ph}}\right)^3 = \frac{4}{3}\pi \frac{1}{\lambda_a^3} \tag{3.39}$$

Jeans has shown that each standing wave formed by photons or phonons can be polarized twice. Taking into account this fact the concentrations of standing photons and standing phonons in the all three directions (1,2,3) are equal to:

$$\begin{aligned} n_p^{1,2,3} &= \tfrac{8}{3}\pi \left(\frac{\nu_{1,2,3}^p}{c^{1,2,3}/n}\right)^3 \\ \bar{n}_{ph}^{1,2,3} &= \tfrac{8}{3}\pi \left(\frac{\bar{\nu}_{1,2,3}^{ph}}{v_{ph}^{1,2,3}}\right)^3 \end{aligned} \tag{3.40a,b}$$

where: [c] and [n] are the light speed in vacuum and refraction index of matter; $v_{ph} = v_s$ - velocity of thermal phonons, equal to sound velocity.

The standing waves B of atoms and molecules have only one linear polarization in directions (1,2,3). Therefore, their concentrations are described by an equation of type (3.39).

According to our model (see Introduction), superposition of each of three differently oriented (1,2,3) standing waves B forms quasi-particles which we have termed *effectons*. They are divided into the most probable (primary) (with zero resulting impulse) and mean (secondary) effectons. Quasiparticles, formed by 3D superposition of standing photons and phonons, originating in the course of ($a \Leftrightarrow b$) and ($\bar{a} \Leftrightarrow \bar{b}$) transitions of the primary and secondary effectons, respectively, are termed primary and secondary *deformons* (Table 1).

Effectons and deformons are the result of thermal *translations (tr) and librations (lb)* of molecules in directions (1,2,3). These quasiparticles are generally approximated by a parallelepiped with symmetry axes (1,2,3).

As far *three coherent standing waves of corresponding nature take part in the construction of each effecton*, it means that the concentration of such quasi-particles must be three times lower than the concentration of standing waves expressed by eq. (3.39). The coherence of molecules in the volume of the effectons and deformons due to partial Bose-condensation is the most important feature of our model, which leads to degeneration of waves B of these molecules.

Finally, we obtain the concentration of primary effectons, primary transitons and convertons:

$$\left(\ n_{ef} \ \right)_{tr,lb} = \frac{4}{9}\pi \left(\frac{\nu^a_{\rm res}}{v^a_{ph}} \right)^3_{tr,lb} = n_t = n_c \tag{3.41}$$

where

$$\nu^a_{\rm res} = (\nu^a_1 \nu^a_2 \nu^a_3)^{1/3}_{tr,lb} \tag{3.42}$$

is the resulting frequency of a-state of the primary effecton; $\nu^a_1, \nu^a_2, \nu^a_3$ are the most probable frequencies of waves B in a-state in directions (1,2,3), which are calculated according to formula (3.5); v^a_{ph} - the resulting phase velocity of effectons in a-state, which corresponds to eq. (3.35).

The *concentration of secondary (mean) effectons and secondary transitons* is expressed in the same way as eq. (3.41):

$$(\bar{n}_{ef})_{tr,lb} = \frac{4}{9}\pi \left(\frac{\bar{\nu}^a_{\rm res}}{\bar{v}^a_{ph}} \right)^3_{tr,lb} = n_t \tag{3.43}$$

where *phase velocity* $\bar{v}^a_{ph}$ corresponds to eq. (3.36);

$$\overline{\nu}^a_{\rm res} = (\bar{\nu}^a_1 \bar{\nu}^a_2 \bar{\nu}^a_3)^{1/3} \tag{3.44}$$

- the resulting frequency of mean waves B in $\bar{a}$-state. The mean values $\bar{\nu}^a_{1,2,3}$ are found by the formula (3.16).

Maximum concentrations of the most probable and mean effectons ($n^{\max}_{ef}$) and ($\bar{n}^{\max}_{ef}$), as well as corresponding concentrations of transitons ($n^{\max}_t$) and ($\bar{n}^{\max}_t$) follow from the requirement that it should not be higher than the concentration of atoms.

If a molecule or *elementary cell* consists of $[q]$ *atoms*, which have their own degrees of freedom and corresponding impulses, then

$$n^{\max}_{ef} = n^{\max}_t = \overline{n}^{\max}_{ef} = \overline{n}^{\max}_t = q\frac{N_0}{V_0}$$

The concentration of the electromagnetic primary deformons from eq. (3.40):

$$\left(\ n_d \ \right)_{tr,lb} = \frac{8}{9}\pi \left(\frac{\nu^{\rm res}_d}{c/n} \right)^3_{tr,lb} \tag{3.46}$$

where (c) and (n) are light speed and refraction index of matter;

$$\left(\ \nu_d^{\rm res} \ \right)_{tr,lb} = \left(\ \nu_p^{(1)} \nu_p^{(2)} \nu_p^{(3)} \ \right)^{1/3}_{tr,lb} \tag{3.47}$$

- the resulting frequency of primary deformons, where

$$\left(\ \nu_p^{1,2,3} \ \right)_{tr,lb} = c \left(\ \tilde{\nu}_p^{1,2,3} \ \right)_{tr,lb} \tag{3.48}$$

are the most probable frequencies of photons with double polarization, related to translations and librations; c - the speed of light; $\tilde{\nu}_p$ - the wave numbers, which may be found from oscillatory spectra of matter.

The *concentration of* acoustic *secondary deformons* derived from eq. (3.40) is:

$$\left(\ \bar{n}_d \ \right)_{tr,lb} = \frac{8}{9}\pi \left(\frac{\bar{\nu}_d^{\rm res}}{v_s} \right)^3_{tr,lb} \tag{3.49}$$

where v_s is the sound velocity; and

$$\left(\ \bar{\nu}_d^{\rm res} \ \right)_{tr,lb} = \left(\ \bar{\nu}_{ph}^{(1)} \bar{\nu}_{ph}^{(2)} \bar{\nu}_{ph}^{(3)} \ \right)^{1/3}_{tr,lb} \tag{3.50}$$

is the resulting frequency of *secondary* deformons (translational and librational); in this formula:

$$\left(\ \bar{\nu}_{ph}^{1,2,3} \ \right)_{tr,lb} = \left| \ \bar{\nu}^a - \bar{\nu}^b \ \right|^{1,2,3}_{tr,lb} \tag{3.51}$$

are the frequencies of secondary phonons in directions (1,2,3), calculated from (3.16) and (3.17).

Since the primary and secondary deformons are the results of transitions ($a \Leftrightarrow b$ and $\bar{a} \Leftrightarrow \bar{b}$)$_{tr,lb}$ of the primary and secondary effectons, respectively, then the maximum concentration of effectons, transitons and deformons must coincide:

$$n_d^{\max} = \overline{n}_d^{\max} = n_{ef}^{\max} = n_t^{\max} = \overline{n}_{ef}^{\max} = \overline{n}_t^{\max} = q\frac{N_0}{V_0} \tag{3.52}$$

4. HIERARCHIC THERMODYNAMICS

4.1. The internal energy of matter as a hierarchical system of collective excitations

The quantum theory of crystal heat capacity leads to the following equation for the density of thermal internal energy (Ashkroft, Mermin, 1976):

$$\epsilon = \frac{1}{V}\frac{i\sum E_i \exp(-E_i/kT)}{i\sum \exp(-E_i/kT)} \tag{4.1}$$

where V - the crystal volume; E_i - the energy of the i-stationary state.

According to our Hierarchic theory, the internal energy of matter is determined by the concentration (n_i) of each type of quasiparticles, probabilities of excitation of each of their states (P_i) and the energies of corresponding states (E_i). The condensed matter is considered as an "ideal gas" of 3D standing waves of different types (quasiparticles and collective excitations). However, the dynamic equilibrium between types of quasiparticles is very sensitive to the external and internal perturbations.

The total partition function - the sum of the relative probabilities of excitation of all states of quasiparticles is equal to:

$$Z = \sum_{tr,lb} \left\{ \begin{array}{c} \left(P^a_{ef} + P^b_{ef} + P_d\right) + \\ + \left(\bar{P}^a_{ef} + \bar{P}^b_{ef} + \bar{P}_d\right) + \\ + \left[\left(P^A_M + P^B_M\right) + P^M_D\right] \end{array} \right\}_{tr,lb} +$$

$$+ \left(P_{ac} + P_{bc} + P_{\mathrm{cMd}}\right) + \left(P^A_S + P^B_S + P^s_{D^*}\right) \tag{4.2}$$

Here we take into account that the probabilities of excitation of primary and secondary transitons and deformons are the same ($P_d = P_t$; $\bar{P}_d = \bar{P}_t$) and related to the same processes:

$$(a \Leftrightarrow b)_{tr,lb} \quad \text{and} \quad (\bar{a} \Leftrightarrow \bar{b})_{tr,lb} \ \text{ transitions.}$$

The analogous situation is with probabilities of *a, b and cM convertons* and corresponding acoustic deformons excitations: P_{ac}, P_{bc} and $P_{\mathrm{cMd}} = P_{\mathrm{cMt}}$. So it is a reason for taking them into account in the partition function only ones.

The final formula for the total internal energy of (U_{tot}) of one mole of matter leading from mesoscopic model, considering the system of 3D standing waves as an ideal gas is:

$$U_{\mathrm{tot}} = V_0 \frac{1}{Z} \sum_{tr,lb} \left\{ \left[\begin{array}{c} n_{ef} \left(\ P^a_{ef}E^a_{ef} + P^b_{ef}E^b_{ef} + P_tE_t \ \right) \\ + n_dP_dE_d \end{array} \right] + \right.$$

$$+ \left[\bar{n}_{ef} \left(\ \bar{P}^a_{ef}\bar{E}^a_{ef} + \bar{P}^b_{ef}\bar{E}^b_{ef} + \bar{P}_t\bar{E}_t \ \right) + \bar{n}_d\bar{P}_d\bar{E}_d\right] +$$

$$\left. + \left[n_M \left(\ P^A_ME^A_M + P^B_ME^B_M \ \right) + n_DP^D_ME^D_M\right]_{tr,lb} + \right.$$

$$+V_0\frac{1}{Z}\left[n_{\rm con}\left(\ P_{ac}E_{ac}+P_{bc}E_{bc}+P_{\rm cMt}E_{\rm cMt}\ \right)+\right.$$

$$\left.+\ \ (n_{\rm cda}P_{ac}E_{ac}+n_{\rm cdb}P_{bc}E_{bc}+n_{\rm cMd}P_{\rm cMd}E_{\rm cMd})\ \right]+$$

$$+V_0\frac{1}{Z}n_s\left[\ \left(\ P_S^{A^*}E_S^{A^*}+P_S^{B^*}E_S^{B^*}\ \right)\ +n_{D^*}P_S^{D^*}E_S^{D^*}\ \right] \tag{4.3}$$

where all types the effecton's contributions in total internal energy correspond to:

$$U_{ef}=V_0\frac{1}{Z}\sum_{tr,lb}\left[\ n_{ef}\ \ \left(\ P_{ef}^aE_{ef}^a+P_{ef}^bE_{ef}^b\ \right)+\right.$$

$$\left.+\bar{n}_{ef}\left(\ \bar{P}_{ef}^a\bar{E}_{ef}^a+\bar{P}_{ef}^b\bar{E}_{ef}^b\ \right)+n_M\ \ \left(\ P_M^AE_M^A+P_M^BE_M^B\ \right)\ \right]_{tr,lb}+$$

$$+V_0\frac{1}{Z}n_s\left(\ P_s^{A^*}E_s^{A^*}+P_s^{B^*}P_s^{B^*}\ \right) \tag{4.4}$$

all types of deformons contribution in $U_{\rm tot}$ is:

$$U_d=\begin{array}{c}V_0\frac{1}{Z}\sum\limits_{tr.lb}\left(\ n_dP_dE_d+\bar{n}_d\bar{P}_d\bar{E}_d+n_MP_M^DE_M^D\ \right)_{tr,lb}+\\ +V_0\frac{1}{Z}\ n_sP_S^{D^*}E_S^{D^*}\end{array} \tag{4.5}$$

and contribution, related to $[lb/tr]$ convertons:

$$U_{\rm con}=V_0\frac{1}{Z}\left[\ n_{\rm con}\left(\ P_{ac}E_{ac}+P_{bc}E_{bc}+P_{\rm cMt}E_{\rm cMt}\ \right)\ +\right.$$

$$\left.+\ \ (n_{\rm cda}P_{ac}E_{ac}+n_{\rm cdb}P_{bc}E_{bc}+n_{\rm cMd}P_{\rm cMt}E_{\rm cMd})\ \right] \tag{4.5a}$$

Contributions of all types of transitons (U_t) also can be easily calculated.

The intramolecular configurational dynamics of molecules is automatically taken into account in our approach as it has an influence on the intermolecular dynamics, dimensions, and on concentration of quasiparticles as well as on the energy of excitation of their states. These dynamics affects the positions of the absorption bands in oscillatory spectra and values of sound velocity, that we use for calculation of internal energy.

The remnant small contribution of intramolecular dynamics to $\rm U_{tot}$ is related to oscillation energy corresponding to fundamental molecular modes (ν_p^i). It may be estimated using Plank distribution:

$$U_{\rm in}=N_0\sum_1^i h\bar{\nu}_p^i=N_0\sum_1^i h\nu_p^i\left[\ \exp\left(\ h\nu_p^i/kT\ \right)-1\ \right]^{-1} \tag{4.5b}$$

where (i) is the number of internal degrees of freedom.

$i=3q-6$ for nonlinear molecules; $i=3q-5$ for linear molecules

q is the number of atoms forming a molecule.

It has been shown by our computer simulations for the case of water and ice that $U_{\rm in}\ll U_{\rm tot}$. It should be general condition for any condensed matter.

Let us consider now the meaning of the variables in formulae (4.2 - 4.5), necessary for the internal energy calculations:

V_0 is the molar volume;

$n_{ef,}$ $\bar{n}_{ef}$ are the concentrations of primary (eq. 3.41) and secondary (eq. 3.42) effectons; E^a_{ef}, E^b_{ef} are the energies of the primary effectons in a and b states:

$$\left[\ E^a_{ef} = 3h\nu^a_{ef}\ \right]_{tr,lb} \tag{4.6}$$

$$\left[\ E^b_{ef} = 3h\nu^b_{ef}\ \right]_{tr,lb}, \tag{4.7}$$

where

$$\left[\ \nu^a_{ef} = \tfrac{1}{3}\left(\ \nu^a_1 + \nu^a_2 + \nu^a_3\ \right)\ \right]_{tr,lb} \tag{4.8}$$

$$\left[\ \nu^b_{ef} = \tfrac{1}{3}\left(\ \nu^b_1 + \nu^b_2 + \nu^b_3\ \right)\ \right]_{tr,lb} \tag{4.9}$$

are the **characteristic frequencies** of the primary effectons in the (a) and (b) - states;

$\nu^a_{1,2,3}$, $\nu^b_{1,2,3}$ are determined according to formulas (3.5 and 3.6);

P^a_{ef}, P^b_{ef} - the relative probabilities of excitation (thermoaccessibilities) of effectons in (a) and (b) states [2-4] introduced as:

$$\left[P^a_{ef} = \exp\left(-\frac{\left|E^a_{ef} - E_0\right|}{kT}\right) = \exp\left(-\frac{3h\left|\nu^a_{ef} - \nu_0\right|}{kT}\right)\right]_{tr,lb} \tag{4.10}$$

$$\left[P^b_{ef} = \exp\left(-\frac{\left|E^a_{ef} - E_0\right|}{kT}\right) = \exp\left(-\frac{3h\left|\nu^b_{ef} - \nu_0\right|}{kT}\right)\right]_{tr,lb} \tag{4.11}$$

where

$$E_0 = 3kT = 3h\nu_0 \tag{4.12}$$

is the equilibrium energy of all types of quasiparticles determined by the temperature of matter (T):

$$\nu_0 = \frac{kT}{h} \tag{4.13}$$

is the equilibrium frequency.

$\bar{E}^a_{ef}$, $\bar{E}^b_{ef}$ are the characteristic energies of secondary effectons in $\bar{a}$ and $\bar{b}$ states:

$$\left[\ \bar{E}^a_{ef} = 3h\bar{\nu}^a_{ef}\ \right]_{tr,lb} \tag{4.14}$$

$$\left[\ \bar{E}^b_{ef} = 3h\bar{\nu}^b_{ef}\ \right]_{tr,lb}, \tag{4.15}$$

where

$$\left[\ \bar{\nu}^a_{ef} = \tfrac{1}{3}\left(\ \bar{\nu}^a_1 + \bar{\nu}^a_2 + \bar{\nu}^a_3\ \right)\ \right]_{tr,lb} \tag{4.16}$$

$$\left[\ \bar{\nu}^b_{ef} = \tfrac{1}{3}\left(\ \bar{\nu}^b_1 + \bar{\nu}^b_2 + \bar{\nu}^b_3\ \right)\ \right]_{tr,lb} \tag{4.17}$$

are the characteristic frequencies of mean effectons in $\bar{a}$ and $\bar{b}$ states; $\bar{\nu}^a_{1,2,3}, \bar{\nu}^b_{1,2,3}$ determined according to formulae (3.16 and 3.17).

$\bar{P}^a_{ef}, \bar{P}^b_{ef}$ are the relative probabilities of excitation (thermoaccessibilities) of mean effectons in $\bar{a}$ and $\bar{b}$ states (Kaivarainen, 1989a) introduced as:

$$\left[\bar{P}^a_{ef} = \exp\left(-\frac{\left|\bar{E}^a_{ef} - E_0\right|}{kT}\right) = \exp\left(-\frac{3h\left|\bar{\nu}^a_{ef} - \nu_0\right|}{kT}\right)\right]_{tr,lb} \tag{4.18}$$

$$\left[\bar{P}^b_{ef} = \exp\left(-\frac{\left|\bar{E}^a_{ef} - E_0\right|}{kT}\right) = \exp\left(-\frac{3h\left|\bar{\nu}^b_{ef} - \nu_0\right|}{kT}\right)\right]_{tr,lb} \tag{4.19}$$

Parameters of deformons (primary and secondary) [tr and lb]:

n_d, $\bar{n}_d$ are the concentrations of primary (eq. 3.46) and secondary (eq. 3.49) deformons;

E_d, $\bar{E}_d$ are the characteristic energies of the *primary* and *secondary* deformons, equal to energies of primary and secondary transitons:

$$\left[\ E_d = 3h\nu^{\rm res}_d = E_t\ \right]_{tr,lb} \tag{4.20}$$

$$\left[\ \bar{E}_d = 3h\bar{\nu}^{\rm res}_d = \bar{E}_t\ \right]_{tr,lb} \tag{4.20}$$

where: characteristic frequencies of the primary and secondary deformons are equal to:

$$\left[\ \nu^{\rm res}_d = \tfrac{1}{3}\left(\ \nu^{(1)}_p + \nu^{(2)}_p + \nu^{(3)}_p\ \right)\ \right]_{tr,lb} \tag{4.22}$$

$$\left[\ \bar{\nu}_d^{\rm res} = \tfrac{1}{3} \left(\ \bar{\nu}_{ph}^{(1)} + \bar{\nu}_{ph}^{(2)} + \bar{\nu}_{ph}^{(3)} \ \right) \ \right]_{tr,lb} \tag{4.23}$$

The frequencies of the primary photons are calculated from the experimental data of oscillatory spectra using (3.48).

The frequencies of *secondary phonons* are calculated as:

$$\left(\ \overline{\nu_{ph}^{1,2,3}} \ \right)_{tr,lb} = \ |\overline{\nu}_a - \overline{\nu}_b|_{tr,lb}^{1,2,3} \tag{4.24}$$

where $\overline{\nu_a^{1,2,3}}$ and $\overline{\nu_b^{1,2,3}}$ are founded in accordance with (3.16) and (3.17).

P_d and $\bar{P}_d$ are the relative probabilities of excitation of primary and secondary deformons in medium, surrounding effectons, introduced as the probabilities of intermediate transition states:

$$(a \Leftrightarrow b)_{tr,lb} \ \text{ and } \ (\bar{a} \Leftrightarrow \bar{b})_{tr,lb} :$$

$$\left(\ P_d = P_{ef}^a \cdot P_{ef}^b \ \right)_{tr,lb} \tag{4.25}$$

$$\left(\ \bar{P}_d = \bar{P}_{ef}^a \cdot \bar{P}_{ef}^b \ \right)_{tr,lb} \tag{4.26}$$

Parameters of transitons [tr and lb]

$(n_t)_{tr,lb}$ and $(\bar{n}_t)_{tr,lb}$ are concentrations of primary and secondary transitons, equal to concentration of primary (3.41) and secondary (3.43) effectons:

$$(n_t = n_{ef})_{tr,lb}; \quad (n_t = n_{ef})_{tr,lb} \tag{4.27}$$

$(P_t$ and $\bar{P}_t)_{tr,lb}$ are the relative probabilities of excitation of primary and secondary transitons, equal to that of primary and secondary deformons:

$$(P_t = P_d)_{tr,lb}; \quad (\bar{P}_t = \bar{P}_d)_{tr,lb}$$

$(E_t$ and $\bar{E}_t)_{tr,lb}$ are the energies of primary and secondary transitons:

$$\left[\ E_t = E_d = h(\nu_p^{(1)} + \nu_p^{(2)} + \nu_p^{(3)}) \ \right]_{tr,lb} \tag{4.28}$$

$$\left\{ \ \bar{E}_t = \bar{E}_d = 3h \left[\ | \ \bar{\nu}_{ef}^a - \nu_0 \ | + | \ \bar{\nu}_{ef}^b - \nu_0 \ | \ \right]^{1,2,3} \ \right\}_{tr,lb} \tag{4.29}$$

Primary and secondary deformons in contrast to transitons, represent the quasi-elastic mechanism of the effectons interaction via medium.

Parameters of macroeffectons [tr and lb]

$(n_M = n_d)_{tr,lb}$ are the concentrations of macroeffectons equal to that of primary deformons (3.46);

(E_M^A and $E_M^B)_{tr,lb}$ are the energies of A and B states of macroeffectons; (ν_M^A and $\nu_M^B)_{tr,lb}$ are corresponding frequencies, defined as:

$$\left[E_M^A = 3h\nu_M^A = -kT\ln P_M^A\right]_{tr,lb} \tag{4.29a}$$

$$\left[E_M^B = 3h\nu_M^B = -kT\ln P_M^B\right]_{tr,lb} \tag{4.29b}$$

where

$$\left[P_M^A = P_a \cdot \overline{P}_a\right]_{tr,lb} \tag{4.29c}$$

and

$$\left[P_M^B = P_b \cdot \overline{P}_b\right]_{tr,lb} \tag{4.29d}$$

are the relative probabilities of excitation of A and B states of macroeffectons.

Parameters of macrodeformons [tr and lb]

$(n_M^D)_{tr,lb}$ is the concentration of macrodeformons equal to that of macroeffectons (macrotransitons) corresponding to concentration of corresponding primary deformons: see eq.(3.46);

$$(P_M^D)_{tr,lb} = (P_M^A \cdot P_M^B)_{tr,lb} \tag{4.29e}$$

are the probabilities of macrodeformons excitation;

$$(E_D^M)_{tr,lb} = -kT\ln(P_M^D)_{tr,lb} = 3h(\nu_M^D)_{tr,lb} \tag{4.29f}$$

are the energies of macrodeformons;

Parameters of convertons and related excitations

The frequency and energy of a-convertons and b- convertons:

$$\nu_{ac} = \mid (\nu_{ef}^a)_{lb} - (\nu_{ef}^a)_{tr} \mid; \qquad E_{ac} = 3h\nu_{ac}$$

$$\nu_{bc} = \mid (\nu_{ef}^b)_{lb} - (\nu_{ef}^b)_{tr} \mid; \qquad E_{bc} = 3h\nu_{bc} \tag{4.30}$$

where: characteristic frequencies $(\nu_{ef}^a)_{lb}$ and $(\nu_{ef}^a)_{tr}$ correspond to (4.8).

where characteristic frequencies $(\nu_{ef}^b)_{lb}$ and $(\nu_{ef}^b)_{tr}$ correspond to (4.9).

Probabilities of (a) and (b) convertons, equal to that of corresponding acoustic c-deformons excitations:

$$\begin{pmatrix} P_{ac} = (P_{ef}^a)_{tr} \cdot (P_{ef}^a)_{lb} \\ P_{bc} = (P_{ef}^b)_{tr} \cdot (P_{ef}^b)_{lb} \end{pmatrix} \tag{4.30a}$$

Probability and energy of c - Macrotransitons

(*Macroconvertons) excitation* [*simultaneous excitation of (a) and (b) convertons*], *equal to that of c- Macrodeformons is:*

$$P_{\rm cMd} = P_{ac} \cdot P_{bc}; \qquad E_{\rm cMt} = E_{\rm cMd} = -kT \cdot \ln P_{\rm cMd} \tag{4.30b}$$

The characteristic frequency of cM-transitons and cM-deformons is:

$$\nu_{cMt} = \nu_{cMd} = E_{cMd}/3h$$

The concentrations of (a), (b)-convertons ($n_{\rm con}$) and *c*-Macrotransitons ($n_{\rm cMd}$) are equal to that of primary effectons (n_{ef}).

The concentrations of acoustic deformons, excited by convertons

The concentrations of *ca-deformons* and *cb-deformons,* representing 3D standing phonons, excited by *a*-convertons and by *b*-convertons correspondingly are:

$$\left(\ n \ \right)_{\rm cad,cbd} = \frac{8}{9}\pi \left(\frac{\nu_{ac,bc}}{v_s} \right)^3 \tag{4.30c}$$

where $[v_s]$ is the sound velocity and

$$\nu_{ac} = (\nu^a_{ef})_{lb} - (\nu^a_{ef})_{tr}, \quad \nu_{bc} = (\nu^b_{ef})_{lb} - (\nu^b_{ef})_{tr} \tag{4.30d}$$

are characteristic frequencies of *a*- and *b*-convertons, equal to the difference between characteristic frequencies of primary librational and translational effectons (see eqs.4.8 and 4.9) in *a* and *b* states correspondingly.

The concentration of *cM-deformons*, excited by *cM-transitons (or Macroconvertons)* is equal to:

$$n_{\rm cMd} = \frac{8}{9}\pi \left(\frac{\nu_{\rm cMd}}{v_s} \right)^3 \tag{4.30e}$$

where: $\nu_{\rm cMd}$ is characteristic frequency of c-Macrodeformons, equal to that of c-Macrotransitons (Macroconvertons).

The maximum concentration of all convertons-related excitations is also limited by concentration of molecules

Parameters of supereffectons:

$(n_S = n_d)_{lb}$ is the concentration of supereffectons, equal to that of primary librational deformons (3.46);

$P_S^{A^*}$; $P_S^{B^*}$ are the relative probabilities of excitation of A^* and B^*:

$$P_S^{A^*} = (P_M^A)_{tr} \cdot (P_M^A)_{lb} \qquad P_S^{B^*} = (P_M^B)_{tr} \cdot (P_M^B)_{lb} \tag{4.30f}$$

and $E_S^{A^*}$; $E_S^{B^*}$ are the energies of A and B states of supereffectons from (3.27) and (3.28);

$$E_S^{A^*} = -kT \cdot \ln P_S^{A^*} \qquad E_S^{B^*} = -kT \cdot \ln P_S^{B^*}$$

Parameters of superdeformons:

n_{D^*} is the concentration of superdeformons, equal to that of supereffectons;

$$P_S^{D^*} = (P_M^D)_{tr}(P_M^D)_{lb} \tag{4.30g}$$

is the relative probability of superdeformons;
$E_S^{D^*}$ is the energy of superdeformons, defined as:

$$E_S^{D^*} = -kT \ln P_S^{D^*} \tag{4.30h}$$

Substituting the parameters of quasiparticles, calculated in this way into eqs. (4.2 and 4.3), we obtain the **total internal energy** of one mole of matter in solid or liquid phase. For water and ice the theoretical results coincide with experimental one fairly well (see Fig. 2).

It is important that our equations are the same for solid and liquid states. The difference in experimental parameters, such as molar volume, sound velocity, refraction index, positions of translational and librational bands determines the difference of internal energy and of more than 100 another parameters of any state of condensed matter, which can be calculated using eq. (4.3). **It is important to stress that our concept is general for solids and liquids, for crystals, glasses and amorphous matter.**

4.2. The contributions of kinetic and potential energy to the total internal energy

The total internal energy of matter (U^{tot}) is equal to the sum of total kinetic (T^{tot}) and total potential (V^{tot}) energy:

$$U^{\text{tot}} = T^{\text{tot}} + V^{\text{tot}}$$

The kinetic energy of wave B (T_B) of one molecule may be expressed using its total energy (E_B), mass of molecule (m), and its phase velocity as wave B (v_{ph}):

$$T_B = \frac{mv_{gr}^2}{2} = \frac{E_B^2}{2mv_{ph}^2} \tag{4.31}$$

The total mass (M_i) of 3D standing waves B forming effectons, transitons and deformons of different types are proportional to number of molecules in the volume of corresponding quasiparticle ($V_i = 1/n_i$):

$$M_i = \frac{1/n_i}{V_0/N_0} m \tag{4.32}$$

the limiting condition for minimum mass of quasiparticle is:

$$M_i^{\min} = m \tag{4.33}$$

Consequently the kinetic energy of each coherent effectons is equal to

$$\left[T_{\rm kin}^i = \frac{E_i^2}{2M_i v_{ph}^2} \right] \tag{4.34}$$

where: E_i is a total energy of given quasiparticle.

The kinetic energy of coherent primary and secondary deformons and transitons we express analogously to eq. (4.34), but instead of the phase velocity of waves B we use the light speed and resulting sound velocity $v^{\rm res}$ (eq.3.24), respectively:

$$\left[T_{\rm kin}^i = \frac{E_i^2}{2M_i c^2} \right]_d \quad \text{and} \quad \left[\overline{T}_{\rm kin}^i = \frac{E_i^2}{2M_i (v_s^{\rm res})^2} \right]_{\overline{d}} \tag{4.35}$$

The kinetic energies of $[tr/lb]$ convertons:

$$\left[T_{\rm kin}^i = \frac{(E_i/3)^2}{2M_i (v_s^{\rm res})^2} \right] = \left[T_{\rm kin}^i = \frac{E_i^2}{6M_i (v_s^{\rm res})^2} \right]_{con} \tag{4.35a}$$

According to our model, the kinetic energies of the effectons in a and b and also in the $\bar{a}$ and $\bar{b}$ states are equal. Using (4.34) and (4.35) we obtain from eq.(4.3) the total thermal kinetic energy for 1 mole of matter:

$$T^{\rm tot} = V_0 \frac{1}{Z} \sum_{tr,lb} \left\{ \left[n_{ef} \frac{\sum (E^a)^2_{1,2,3}}{2M_{ef}(v_{ph}^a)^2} * \left(P_{ef}^a + P_{ef}^b \right) + \bar{n}_{ef} \frac{\sum \left(\bar{E}^a \right)^2_{1,2,3}}{2M_{ef}(\overline{v}_{ph}^a)^2} * \left(\bar{P}_{ef}^a + \bar{P}_{ef}^b \right) \right] + \right.$$

$$+ \left[n_t \frac{\sum (E_t)^2_{1,2,3}}{2M_t (v_s^{\rm res})^2} P_d + \bar{n}_t \frac{\sum \left(\bar{E}_t \right)^2_{1,2,3}}{2\bar{M}_t (v_s^{\rm res})^2} \bar{P}_d \right] + \left[n_d \frac{\sum (E_d)^2_{1,2,3}}{2M_d c^2} P_d + \bar{n}_d \frac{\sum \left(\bar{E}_d \right)^2_{1,2,3}}{2M_d (v_s^{\rm res})^2} \bar{P}_d \right] +$$

$$\left. + \left[n_M \frac{\left(E_M^A \right)^2}{6M_M (v_{ph}^A)^2} * \left(P_M^A + P_M^B \right) + n_D \frac{\left(E_D \right)^2}{6M_D (v_s^{\rm res})^2} P_D^M \right] \right\}_{tr,lb} +$$

$$+ V_0 \frac{n_{\rm con}}{Z} \left[\frac{\left(E_{ac} \right)^2}{6M_c (v_s^{\rm res})^2} P_{ac} + \frac{\left(E_{bc} \right)^2}{6M_c (v_s^{\rm res})^2} P_{bc} + \frac{\left(E_{\rm cMd} \right)^2}{6M_c (v_s^{\rm res})^2} P_{cMd} \right] +$$

$$V_0 \frac{1}{Z} \left[n_{\rm cda} \frac{\left(E_{ac} \right)^2}{6M_c (v_s^{\rm res})^2} P_{ac} + n_{\rm cdb} \frac{\left(E_{bc} \right)^2}{6M_c (v_s^{\rm res})^2} P_{bc} + \frac{n_{\rm cMd} \left(E_{\rm cMd} \right)^2}{6M_c (v_s^{\rm res})^2} P_{cMd} \right] +$$

$$+ V_0 \frac{1}{Z} \left[n_S \frac{\left(E_S^{A^*} \right)^2}{6M_S \left(v_{ph}^{A^*} \right)^2} * \left(P_S^{A^*} + P_S^{B^*} \right) + n_S \frac{(E_{D^*})^2}{6M_S (v_s^{\rm res})^2} P_S^{D^*} \right] \tag{4.36}$$

where the effective phase velocity of A-state of macroeffectons is introduced as:

$$\left[\frac{1}{v_{ph}^{A}} = \frac{1}{v_{ph}^{a}} + \frac{1}{\bar{v}_{ph}^{a}}\right]_{tr,lb} \rightarrow \left[v_{ph}^{A} = \frac{v_{ph}^{a} \cdot \bar{v}_{ph}^{a}}{v_{ph}^{a} + \bar{v}_{ph}^{a}}\right]_{tr,lb} \tag{4.37}$$

and the effective phase velocity of supereffecton in A*-state:

$$v_{ph}^{A^*} = \frac{(v_{ph}^{A})_{tr} \cdot (v_{ph}^{A})_{lb}}{(v_{ph}^{A})_{tr} + (v_{ph}^{A})_{lb}} \tag{4.38}$$

Total potential energy is defined by the difference between total internal (eq. 4.3) and total kinetic energy (eq. 4.36):

$$V^{tot} = U^{tot} - T^{tot} \tag{4.39}$$

Consequently, we can separately calculate the kinetic and potential energy contributions to the total thermal internal energy of matter, using four experimental parameters, obtained at the same temperature and pressure:

1) *density or molar volume;*
2) *sound velocity;*
3) *refraction index* and
4) *positions of translational and librational bands* in oscillatory spectrum of condensed matter.

It is important to stress that the same equations are valid for liquids and solids.

The contributions of all individual types of quasiparticles in thermodynamics as well as a lot of characteristics of these quasiparticles also may be calculated, using hierarchic theory.

4.3. Some useful parameters of condensed matter

The total **Structural Factor** can be calculated as a ratio of the kinetic to the total energy of matter:

$$SF = T^{\mathrm{tot}}/U^{\mathrm{tot}} \tag{4.40}$$

The structural factors, related to contributions of translations (SFtr) and to librations (SFlb) could be calculated separately as:

$$SFtr = T_{tr}/U^{\mathrm{tot}} \quad \text{and} \quad SFlb = T_{lb}/U^{\mathrm{tot}} \tag{4.41}$$

Dynamic parameters of quasiparticles, introduced in Hierarchic theory

The frequency of c- Macrotransitons or Macroconvertons excitation, representing [dissociation/association] of primary librational effectons - "flickering clusters" as a result of interconversions between primary [lb] and [tr] effectons is:

$$F_{cM} = \frac{1}{\tau_{Mc}} P_{Mc}/Z \tag{4.42}$$

where: $P_{Mc} = P_{ac}P_{bc}$ is a probability of Macroconvertons excitation;
Z is a total partition function (see eq.4.2);
the life-time of Macroconvertons is:

$$\tau_{Mc} = (\tau_{ac}\tau_{bc})^{1/2} \tag{4.43}$$

The cycle-period of (ac) and (bc) convertons are determined by the sum of life-times of intermediate states of primary translational and librational effectons:

$$\begin{array}{c} \tau_{ac} = (\tau_a)_{tr} + (\tau_a)_{lb}; \\ \tau_{bc} = (\tau_b)_{tr} + (\tau_b)_{lb}; \end{array} \tag{4.44}$$

The life-times of primary and secondary effectons (lb and tr) in a- and b-states are the reciprocal values of corresponding state frequencies:

$$[\tau_a = 1/\nu_a; \quad \tau_{\overline{a}} = 1/\nu_{\overline{a}}]_{tr,lb}; \tag{4.45}$$

$$[\tau_b = 1/\nu_b; \quad \tau_{\overline{b}} = 1/\nu_{\overline{b}}]_{tr,lb} \tag{4.45a}$$

$[(\nu_a)$ and $(\nu_b)]_{tr,lb}$ correspond to eqs. 4.8 and 4.9;
$[(\nu_{\overline{a}})$ and $(\nu_{\overline{b}})]_{tr,lb}$ could be calculated using eqs.4.16; 4.17.

The frequency of (ac) and (bc) convertons excitation [lb/tr]:

$$F_{ac} = \frac{1}{\tau_{ac}} P_{ac}/Z \tag{4.46}$$

$$F_{bc} = \frac{1}{\tau_{bc}} P_{bc}/Z \tag{4.47}$$

where: P_{ac} and P_{bc} are probabilities of corresponding convertons excitations (see eq.4.29a).

The frequency of Supereffectons and Superdeformons (biggest fluctuations) excitation:

$$F_{SD} = \frac{1}{(\tau_{A^*} + \tau_{B^*} + \tau_{D^*})} P_S^{D^*}/Z \tag{4.48}$$

It is dependent on cycle-period of Supereffectons: $\tau_{SD} = \tau_{A^*} + \tau_{B^*} + \tau_{D^*}$ and probability of Superdeformons activation ($P_S^{D^*}$), like the limiting stage of this cycle.

The averaged life-times of Supereffectons in A^* and B^* state are dependent on similar states of translational and librational macroeffectons :

$$\tau_{A^*} = [(\tau_A)_{tr}(\tau_A)_{lb}] = [(\tau_a \tau_{\overline{a}})_{tr}(\tau_a \tau_{\overline{a}})_{lb}]^{1/2} \tag{4.49}$$

and that in B state:

$$\tau_{B^*} = [(\tau_B)_{tr}(\tau_B)_{lb}] = [(\tau_b \tau_{\overline{b}})_{tr}(\tau_b \tau_{\overline{b}})_{lb}]^{1/2} \tag{4.50}$$

The life-time of Superdeformons excitation
It is determined by frequency of beats between A* and B*states of Supereffectons as:

$$\tau_{D^*} = 1/\left|(1/\tau_{A^*}) - (1/\tau_{B^*})\right| \tag{4.51}$$

The frequency of $A \rightleftharpoons B$ cycle excitations of translational and librational macroeffectons is defined in a similar way:

$$\left[F_M = \frac{1}{(\tau_A + \tau_B + \tau_D)} P_M^D/Z\right]_{tr,lb} \tag{4.52}$$

where:

$$(\tau_A)_{tr,lb} = [(\tau_a \tau_{\overline{a}})_{tr,lb}]^{1/2} \tag{4.53}$$

and

$$(\tau_B)_{tr,lb} = [(\tau_b \tau_{\overline{b}})_{tr,lb}]^{1/2} \tag{4.54}$$

$$(\tau_D)_{tr,lb} = 1/\left|(1/\tau_A) - (1/\tau_B)\right|_{tr,lb} \tag{4.55}$$

The frequency of primary translational effectons $(a \rightleftharpoons b)_{tr}$ transitions:

$$F_{tr} = \frac{1/Z}{(\tau_a + \tau_b + \tau_t)_{tr}}(P_d)_{tr} \tag{4.56}$$

where: $(P_d)_{tr}$ is a probability of primary translational deformons excitation;

$[\tau_a; \tau_b]_{tr}$ are the life-times of (a) and (b) states of primary *translational* effectons (eq.4.45).

The frequency of primary librational effectons as $(a \rightleftharpoons b)_{lb}$ cycles excitations:

$$F_{lb} = \frac{1/Z}{(\tau_a + \tau_b + \tau_t)_{lb}}(P_d)_{lb} \tag{4.57}$$

where: $(P_d)_{lb}$is a probability of primary librational deformons excitation; τ_a and τ_b are the life-times of (a) and (b) states of primary librational effectons defined as (4.45).

The life-time of primary transitons (tr and lb) as a result of quantum beats between (a) and (b) states of primary effectons could be introduced as:

$$[\tau_t = |1/\tau_a - 1/\tau_b|^{-1}]_{tr,lb} \tag{4.58}$$

The fraction of molecules (Fr) in each selected type of excitation (quasiparticle):

$$Fr(i) = P(i)/Z \tag{4.59}$$

where: $P(i)$ is thermoaccessibility (relative probability) of given excitation and Z is total partition function (4.2).

The concentration of molecules in each selected type of excitation:

$$N_m(i) = Fr(i)(N_A/V_0) = [P(i)/Z](N_A/V_0) \tag{4.60}$$

where: N_A and V_0 are the Avogadro number and molar volume of matter.

The concentration of each type of independent excitations (quasiparticles)

$$N(i) = Fr(i)n(i) = [P(i)/Z]n(i) \tag{4.61}$$

where: n(i) is a concentration of given type (i) of quasiparticles; Fr(i) is a fraction of corresponding type of quasiparticles.

The average distance between centers of i-type of randomly distributed quasiparticles:

$$d(i) = 1/[N(i)]^{1/3} = 1/[(P(i)/Z) \cdot n(i)]^{1/3} \tag{4.62}$$

The ratio of average distance between centers of quasiparticles to their linear dimension $[l = 1/n(i)^{1/3}]$:

$$rat(i) = 1/[(P(i)/Z)]^{1/3} \tag{4.63}$$

The number of molecules in the edge of primary translational and primary librational effectons:

$$\kappa^{tr} = \left(V_{ef}^{tr}/v_m\right)^{1/3} = \left[(1/n_{ef}^{tr})/(V_0/N_A)\right]^{1/3} \tag{4.63a}$$

$$\kappa^{lb} = \left(V_{ef}^{lb}/v_m\right)^{1/3} = \left[(1/n_{ef}^{lb})/(V_0/N_A)\right]^{1/3} \tag{4.63b}$$

where: $(1/n_{ef}^{tr,lb})$ is the volume of primary translational or librational effectons; (V_0/N_A) is the volume, occupied by one molecule in condensed matter.

A lot of other parameters, characterizing different physical properties of condensed matter are also possible to calculate, using Hierarchic theory and our **computer program elaborated,** as will be shown in the next chapters.

5. QUANTITATIVE VERIFICATION OF HIERARCHIC THEORY ON EXAMPLES OF ICE AND WATER

All the calculations, based on Hierarchic theory, were performed on the personal computers. The special software: "Comprehensive analyzer of matter properties" [copyright 1997, Kaivarainen] was worked out. This program allows to evaluate more than three hundred parameters of any condensed matter if the following basic experimental data are available in the temperature interval of interest:

1. Positions of translational and librational bands in IR spectra;
2. Sound velocity;
3. Molar volume;
4. Refraction index.

The basic experimental parameters for ice:

The wave numbers $(\tilde{\nu}_{tr})$, corresponding to positions of translational and librational bands in oscillatory IR spectra were taken from book of Eisenberg and Kauzmann (1969). Wave numbers *for ice* at 0^oC are:

$$\left(\tilde{\nu}_{ph}^{(1)}\right)_{tr} = 60cm^{-1};$$
$$\left(\tilde{\nu}_{ph}^{(2)}\right)_{tr} = 160cm^{-1};$$
$$\left(\tilde{\nu}_{ph}^{(3)}\right)_{tr} = 229cm^{-1}$$

Accordingly to our model, the IR photons with corresponding frequencies are irradiated and absorbed a result of $(a \Leftrightarrow b)$ primary translational deformons in ice. Temperature shifts of these bands positions are close to zero:

$$\partial\left(\tilde{\nu}_{ph}^{1,2,3}\right)_{tr}/\partial T \approx 0$$

Wave numbers of *librational* IR bands, corresponding to absorption of photons, related to $(a \Leftrightarrow b)_{lb}^{1,2,3}$ transitions of primary librational effectons of ice are:

$$\left(\tilde{\nu}_{ph}^{(1)}\right)_{lb} = \left(\tilde{\nu}_{ph}^{(2)}\right)_{lb} = \left(\tilde{\nu}_{ph}^{(3)}\right)_{lb} \approx 795cm^{-1}.$$

The equality of wave numbers for three directions (1,2,3) *indicate the spatial isotropy of the librations of* H_2O molecules. In this case deformons and effectons have a cube geometry. In general case they have a shape of parallelepiped (like quasiparticles of translational type) *with each of three ribs, corresponding to most probable de Broglie wave length in selected direction.*

The temperature shift of the position of the librational band maximum for ice is:

$$\partial\left(\tilde{\nu}_{ph}^{1,2,3}\right)_{lb}/\partial T \approx -0.2cm^{-1}/C^0$$

The resulting thermal phonons velocity in ice, responsible for secondary acoustic deformons, is taken as equal to the transverse sound velocity (Johri and Roberts, 1990):

$$v_s^{\text{res}} = 1.99 \cdot 10^5 cm/s$$

This velocity and molar ice volume (V_0) are almost independent on temperature (Eisenberg, 1969):

$$V_0 = 19.6cm^3/M \simeq \text{ const}$$

The basic experimental parameters for Water

The wave numbers of translational bands in IR spectrum, corresponding to quantum transitions of primary translational effectons between *acoustic (a) and*

optical (b) states with absorption or emission of photons, forming electromagnetic 3D translational deformons *at* 0^0C are (Eisenberg, 1969):

$$\left(\tilde{\nu}_{ph}^{(1)}\right)_{tr} = 60cm^{-1}; \quad \left(\tilde{\nu}_{ph}^{(2)}\right)_{tr} \approx \left(\tilde{\nu}_{ph}^{(3)}\right)_{tr} \approx 199cm^{-1}$$

with temperature shifts:

$$\partial\left(\tilde{\nu}_{ph}^{(1)}\right)_{tr}/\partial T = 0; \quad \partial\left(\tilde{\nu}_{ph}^{(2,3)}\right)_{tr}/\partial T = -0.2cm^{-1}/C^0$$

The primary librational deformons of water at 0^0C are characterized by following degenerated wave numbers of librational bands in it IR spectrum:

$$\left(\ \tilde{\nu}_{ph}^{(1)}\ \right)_{lb} \approx \left(\ \tilde{\nu}_{ph}^{(2)}\ \right)_{lb} \approx \left(\ \tilde{\nu}_{ph}^{(3)}\ \right)_{lb} = 700cm^{-1}$$

with temperature shift:

$$\partial\left(\tilde{\nu}_{ph}^{1,2,3}\right)_{lb}/\partial T = -0.7cm^{-1}/C^0$$

Wave numbers are related to the frequencies (ν) of corresponding transitions via light velocity as: $\nu = c\tilde{\nu}$

The dependence of *sound velocity* (v_s) *in water* on temperature within the temperature range $0 - 100^0C$ is expressed by the polynomial (Fine and Millero, 1973):

$$v_s = 1402.385 + 5.03522t - 58.3087 \cdot 10^{-3}t^2 +$$
$$+ 345.3 \cdot 10^{-6}t^3 -$$

$$-1645.13 \cdot 10^{-9}t^4 + 3.9625 \cdot 10^{-9}t^5 \ (m/s).$$

The temperature dependence of molar volume (V_0) of *water* within the same temperature range can be calculated using the polynomial (Kell, 1975; Kikoin, 1976):

$$V_0 = 18000/[(999,83952 + 16.945176t -$$
$$- 7.98704 \cdot 10^{-3}t^2 -$$

$$- 4.6170461 \cdot 10^{-5}t^3 + 1.0556302 \cdot 10^{-7}t^4 -$$
$$- 2.8054253 \cdot 10^{-10}t^5)/$$

$$/(1 + 1.687985 \cdot 10^{-2}t)] \quad (cm^3/M)$$

The *refraction index* for ice was taken as an independent of temperature ($n_{\text{ice}} = 1.35$) and that for water as a variable, depending on temperature in accordance with experimental data, presented by Frontas'ev and Schreiber (1966).

The refraction index for water at 20^0C is approximately:

$$n_{H_2O} \simeq 1.33$$

The temperature dependences of different parameters for ice and water, computed using the formulas of our mesoscopic theory, are presented in Figs.(1-4). It is only a small part of available information. In principle, it is possible to calculate about 200 different parameters for liquid and solid state of any condensed matter [3].

5.1. Discussion of theoretical temperature dependences and comparison with experimental data

It will be shown below that our hierarchic theory makes it possible to calculate unprecedented big amount of parameters for liquids and solids. Those of them that where measured experimentally and taken from literature are in excellent correspondence with theory.

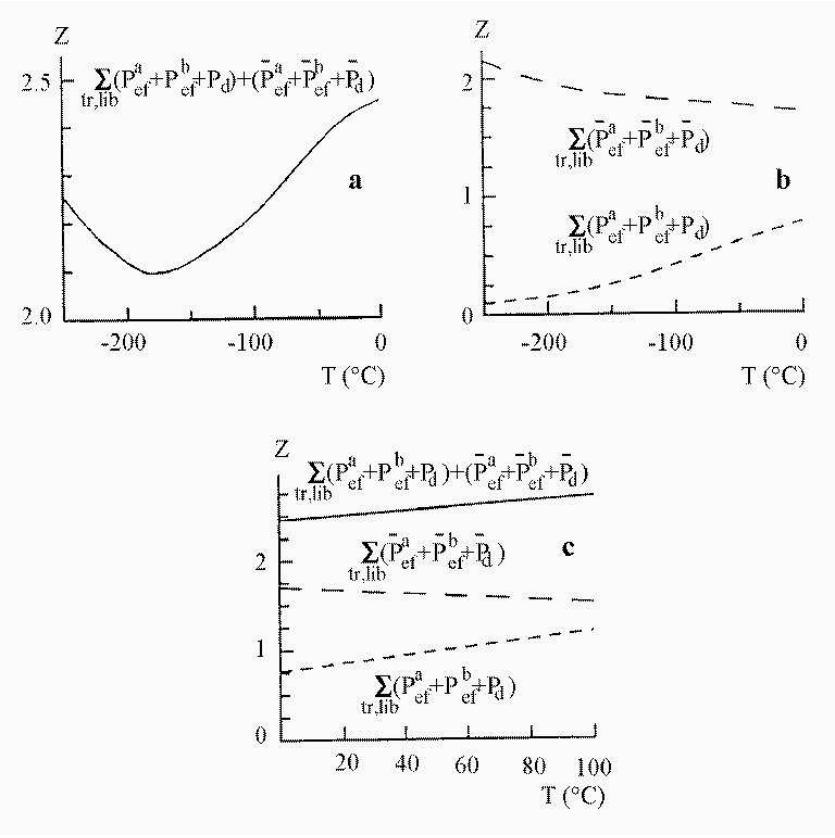

Fig. 1. (a, b, c). Temperature dependences of the resulting thermoaccessibility (Z) (eq.4.2) and contributions related to primary and secondary effectons and deformons for ice (a,b) and water (c).

The resulting thermoaccessibility minimum (Fig. 1a) for ice (Z) corresponds to the temperature of -170^{0}C. The interval from -198 to -173^{0}C is known indeed as anomalies one due to the fact that the heat equilibrium of ice establishes very slowly in the above range (Maeno, 1988). This fact can be explained by the less probable ice structure (minimum value of partition function Z) near -170^0C.

For the other hand, experimental anomaly, related with **maximum** heat capacity (C_p), also is observed near the same temperature. It can be explained, if we present heat capacity as:

$$C_p = \frac{\partial}{\partial T}(\frac{1}{Z}U^*) = -\frac{1}{Z^2}\frac{\partial Z}{\partial T}U^* + \frac{1}{Z}\frac{\partial U^*}{\partial T}$$

One can see, that heat capacity is maximal, when $(\partial Z/\partial T) = 0$ and Z is minimal. It is a condition of Z(T) extremum, just leading from our theory at -170^{0}C (Fig.1a).

In liquid water the temperature dependences of Z and its components are linear. The thermoaccessibility of mean secondary effectons in water decreases, while that of primary effectons increases with temperature, just like in ice (Fig. 1 b,c).

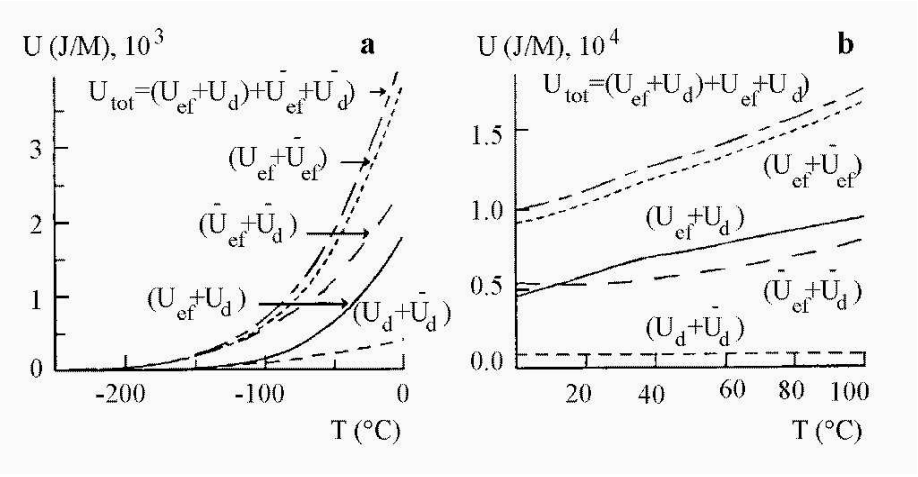

Fig. 2. (a,b). Temperature dependences of the total internal energy ($U_{\rm tot}$) and different contributions for ice (a) and water (b) (eqs. 4.3 - 4.5). Following contributions to $U_{\rm tot}$ are presented:

($U_{ef} + \bar{U}_{ef}$) is the contribution of primary and secondary effectons; ($U_d + \bar{U}_d$) is the contribution of primary and secondary deformons; ($U_{ef} + U_d$) is the contribution of primary effectons and deformons;

($\bar{U}_{ef} + \bar{U}_d$) is the contribution of secondary effectons and deformons.

It leads from our calculations, that contributions of macro- and supereffectons to the total internal energy and that of macro- and superdeformons, as

well as all types of convertons, are much smaller than those of primary and secondary effectons and deformons.

On lowering down the temperature the total internal energy of ice (Fig. 2a) and its components decreases with temperature coming closer to absolute zero. The same parameters for water are decreasing almost linearly within the interval $(100-0)^0C$ (Fig. 2b).

In computer calculations, the values of $C_p(t)$ can be determined by differentiating $U_{\rm tot}$ numerically at any of temperature interval.

It follows from Fig. 2a that the mean value of heat capacity for ice in the interval from -75 to 0^oC is equal to:

$$\bar{C}_p^{ice} = \frac{\Delta U_{\rm tot}}{\Delta T} \approx 39 J/M\,K = 9.3 \text{ cal}/M\,K$$

For water within the whole range $\Delta T = 100^0C$, the change in the internal energy is: $\Delta U = 17 - 9.7 = 7.3 kJ/M$ (Fig.2b). This corresponds to mean value of heat capacity of water:

$$C_p^{water} = \frac{\Delta U_{\rm tot}}{\Delta T} = 73\ J/M\,K = 17.5\ cal/M\,K$$

These results of our theory agree well with the experimental mean values $C_p = 18$ Cal$/M\,K$ for water and $C_p = 9 cal/M\,K$ for ice.

Mesoscopic molecular Bose condensation at physiological temperature: possible or not?

The possibility of existence of mesoscopic (intermediate between microscopic and macroscopic) Bose condensation in form of coherent clusters in condensed matter at the ambient temperature was rejected for a long time. The reason of such shortcoming was a **wrong primary assumption,** that the thermal oscillations of atoms and molecules in condensed matter are the **harmonic** ones (see for example: Beck and Eccles, 1992). The condition of harmonic oscillations means that the averaged kinetic ($\overline{T}_k$) and potential ($\overline{V}$) energy of molecules are equal to each other and linearly dependent on temperature (T).

This condition leads from Virial theorem (Clausius, 1870) for the case of classical systems:

$$\overline{T}_k = \overline{V} = \frac{1}{2} kT \tag{5.1}$$

The averaged kinetic energy of the oscillating particle may be expressed via its averaged impulse (p) and mass (m):

$$\overline{T}_k = \overline{p}^2/2m \tag{5.1a}$$

The most probable wave B length (λ_B) of such particle, based on assumption (5.1), is**:**

$$\lambda_B = h/p = h/(mkT)^{1/2} \tag{5.2}$$

It leads from this formula that around the melting point of ice: $T = 273K$ the value of λ_B is less than 1Å and much less than the approximate distance between centers of molecules ($l \tilde{} 3$Å) in ice and water:

$$\lambda_B < l \tag{5.2a}$$

This result leads to wrong conclusion that water and ice are classical systems, where Bose condensation (BC) is impossible. The same wrong conclusion, based on 5.1 and 5.2 follows for any condensed matter at T around its melting point.

The BC is possible only at conditions, when the wave B of particles is equal or bigger, than the average distance between their centers (l):

$$\lambda_B \geq l = (V_0/N_0)^{1/3} \tag{5.2b}$$

In contrast to low-temperature **macroscopic** BC, accompanied superconductivity and superfluidity, the condition of **mesoscopic** high temperature BC may be expressed as:

$$L > \lambda_B > l \tag{5.2c}$$

where L is a macroscopic parameter, comparable with dimensions of the whole sample.

Condition of partial or mesoscopic BC (5.2c) is general for any liquids and solids as confirmed by our theory and computer simulations for water and ice.

Correct comparisons of ratio between average kinetic and potential energy of matter and applying to Virial theorem may give a right answer to question: is this system classical or quantum ?

It leads from our theoretical dependencies, presented at Fig. $3\,a, b$ that the total kinetic energy of water ($T_{\rm kin}$) is approximately 30 times less than the potential energy (V_p) at the same temperatures. In the case of ice, they differ even more: $(T_{\rm kin}/V) < 1/100$. The resulting $T_{\rm kin}$of water increases almost twice over the range $(0 - 100^0 C)$: from 313 to $585 J/M$. However, the change of the total internal energy ($U_{\rm tot} = T_{\rm kin} + V_p$) is determined mainly by the change in potential energy $V_p(t)$ of ice and water.

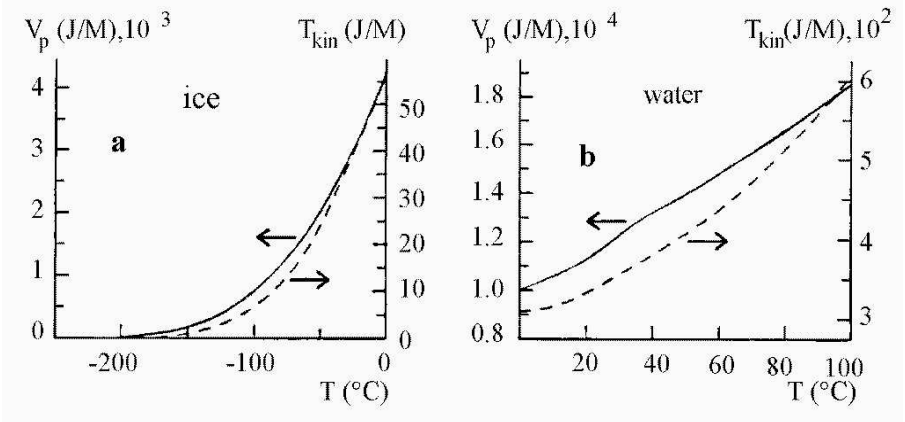

Fig. 3. (a,b). Temperature dependences of the kinetic ($T_{\rm kin}$) and potential (V_p) energy for the ice (a) and water (b), calculated, using eqs.(4.36), .(4.39). . Note that $U_{\rm tot} = T_{\rm kin} + V_p$ and was calculated from eq.(4.3).

We can analyze the above ratio between total kinetic and potential energies in terms of the *Viral theorem worked out by Clausius* (Clausius, 1870; see also Prokhorov, 1988). It is important to note, that this theorem is valid for both: classical and quantum-mechanical systems.

This famous theorem for a system of any kind of particles system - relates the averaged kinetic $\bar{T_k}(\vec{v}) = \sum_i \overline{m_i v_i^2/2}$ and potential $\bar{V}(r)$ energies in the form:

$$2\bar{T_k}(\vec{v}) = \sum_i \overline{m_i v_i^2} = \sum_i \overline{\vec{r_i}\partial V/\partial \vec{r_i}} \tag{5.2d}$$

The potential energy $V(r)$ is a homogeneous **n-order function** like:

$$V(r) \sim r^n \tag{5.3}$$

where the value of power (n) is equal to ratio of doubled average kinetic energy to average potential energy:

$$n = \frac{2\overline{T_k(\vec{v})}}{\overline{V(r)}} \tag{5.3a}$$

For example, for a harmonic oscillator: $n = 2$ and $\bar{T_k} = \bar{V}$. For Coulomb interaction: $n = -1$ and $\bar{T} = -\bar{V}/2$.

For water our calculation of T_k and V gives: $n_w \sim 1/15$ and for ice: $n_{\rm ice} \sim 1/50$. It follows from (5.1) that in water and ice the dependence of potential energy on distance (r) is very weak:

$$V_w(r) \sim r^{(1/15)}; \quad V_{\rm ice} \sim r^{(1/50)} \tag{5.4}$$

These results can be considered as indication of distant interactions in water and ice, as an associative cooperative systems.

We get here a strong evidence that water and ice can not be considered as a classical systems, following condition (5.1).

It is important also to note, that the direct interrelation exists between the infinitive spatial scale of Bose condensation, determined by wave B length: $\lambda = (h/p) \to \infty$ (eq.5.2) and **condition of nonlocality as independence of potential on distance at** $T_k \to 0;\ p \to 0;\ n \to 0$**:**

$$V(r) \ \to const \tag{5.4a}$$

This result is true not only for real condensed matter systems, but also for systems of virtual particles, forming the vacuum (see: http://arXiv.org/abs/physics/0003001).

5.2. Explanation of temperature anomalies, nonmonotonic T-deviations in aqueous systems

Hierarchic theory is the first one enable to predict and give a clear explanation to deviations of temperature dependencies of some physical parameters of water from monotonic ones.

It clarify also the interrelation between these deviations (transitions) and corresponding temperature anomalies in properties of biosystems, such as large-scale dynamics of proteins, the enzymes activity, dynamic equilibrium of [assembly-disassembly] of microtubules and actin filaments, etc.

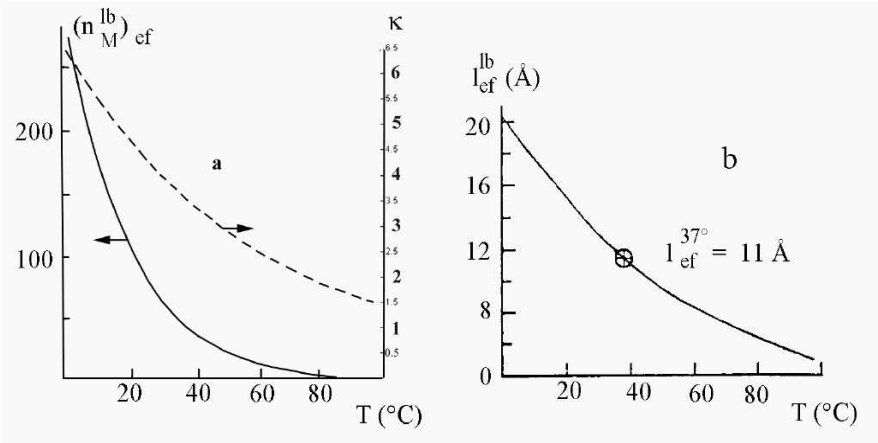

Fig. 4. (a) : The temperature dependencies of the number of H_2O molecules in the volume of primary librational effecton $(n_M^{lb})_{ef}$, left axis) and the number of H_2O per length of this effecton edge (κ, right axis); (b): the temperature dependence of the water primary librational effecton (approximated by cube) edge length $[l_{ef}^{\rm lib} = \kappa(V_0/N_0)^{1/3}]$.

The number of H_2O molecules within the **primary libration effectons** of water, which could be approximated by a cube, decreases from $n_M = 280$ at 0^0 to $n_M \simeq 3$ at 100^0 (Fig. 4a). It should be noted that at physiological temperatures $(35 - 40^0)$ such quasiparticles contain nearly 40 water molecules. This number is close to that of water molecules that can be enclosed in the open interdomain protein cavities judging from X-ray data. The *flickering* of these clusters, i.e. their ($dissociation \rightleftharpoons association$) due to $[lb \Leftrightarrow tr]$ conversions in accordance with our model is directly related to the large-scale dynamics of proteins.

It is important that the linear dimensions of such water clusters (11Å) at physiological temperature are close to dimensions of protein domains (Fig. 4b).

Such spatial correlation indicate that the properties of water exerted a strong influence on the evolution of biopolymers, namely, their dimensions and dynamic properties due to "flickering" of intersubunit water clusters.

We assume here that integer and half-integer values of number of water molecules per effecton's edge [κ] (Fig. 4a) reflect the conditions of increased and

decreased stabilities of water structure correspondingly. It is apparently related to the stability of primary librational effectons as cooperative and coherent water clusters.

Nonmonotonic behavior of water properties with temperature is widely known and well confirmed experimental fact (Drost-Hansen, 1976, 1992; Clegg and Drost-Hansen, 1991; Etzler, 1991; Roberts and Wang, 1993; Roberts and Wang, 1993; Roberts, et al., 1993, 1994; Wang et al., 1994).

We can explain this interesting and important for biological functions phenomenon because of competition between two factors: quantum and structural ones in stability of primary librational effectons.

The quantum factor such as wave B length, determining the value of the effecton edge:

$$\left[l_{ef} = \kappa(V_0/N_0)^{1/3} \tilde{} \lambda_B\right]_{lb} \tag{5.5}$$

decreases monotonously with temperature increasing. The **structural factor** is a sensitive parameter depending on the H_2O effective length: $l_{H_2O} = (V_0/N_0)^{1/3}$ and **their number** $[\kappa]$ in the effecton's edge, approximated by cube.

We suggest that when (l_{ef}) corresponds to *integer* number of H_2O, i.e.

$$[\kappa = (l_{ef}/l_{H_2O}) = 2, 3, 4, 5, 6...]_{lb} \tag{5.6}$$

the *competition* between quantum and structural factors is minimum and primary librational effectons are most stable. On the other hand, when $(l_{ef}/l_{H_2O})_{lb}$ is half-integer, the librational effectons are less stable (the *competition is maximum*). In the latter case $(a \Leftrightarrow b)_{lb}$ equilibrium of the effectons must be shifted rightward - to less stable state of these coherent water clusters. Consequently, the probability of dissociation of librational effectons to a number of much smaller translational effecton, i.e. probability of [lb/tr] convertons increases and concentration of primary librational effectons decreases. Experimentally the nonmonotonic change of this probability with temperature could be registered by dielectric permittivity, refraction index measurements and by that of average density of water. The refraction index change should lead to corresponding variations of surface tension, vapor pressure, viscosity, self-diffusion in accordance to our hierarchic theory (Kaivarainen, 1995, 2000).

In accordance to our model the density of liquid water in composition of librational effectons is lower than the average in the bulk water. In the former case all hydrogen bonds of molecules are saturated like in ideal ice in contrast to latter one.

We can see from Fig.4a that the *number of water molecules in primary lb effecton edge* (κ) is integer near the following temperatures:

$$6^0(\kappa = 6);\ \ 17^0(\kappa = 5);\ \ 32^0(\kappa = 4);\ \ 49^0(\kappa = 3);\ \ 77^0(\kappa = 2) \tag{5.7}$$

These temperatures coincide very well with the *maximums of relaxation time* in pure water and with dielectric response anomalies (Roberts, et al., 1993; 1994; Wang, et al., 1994). The special temperatures predicted by our theory are close also to chemical kinetic (Aksnes, Asaad, 1989; Aksnes, Libnau, 1991), refractometry (Frontas'ev, Schreiber 1966) and IR (Prochorov, 1991) data. Small

discrepancy may result from the high sensitivity of water to any kind of perturbation, guest-effects and additional polarization of water molecules, induced by high frequency visible photons. Even such low concentrations of inorganic ions ester and NaOH as used by Aksnes and Libnau (1991) may change water properties. The increase of H_2O polarizability under the effect of light also may lead to enhancement of water clusters stability and to corresponding high-temperature *shift of nonmonotonic changes of water properties.*

The semi integer numbers of $[\kappa]$ for pure water correspond to temperatures:

$$0^0(\kappa = 6.5);\ \ 12^0(\kappa = 5.5);\ \ 24^0(\kappa = 4.5);\ \ 40^0(\kappa = 3.5); \qquad (5.7a)$$
$$62^0(\kappa = 2.5);\ \ 99^0(\kappa = 1.5)$$

The conditions (5.7a) characterize the less stable water structure than conditions (5.7). The first order phase transitions - freezing at 0^0 and boiling at 100^0 of water almost exactly correspond to $\kappa = 6.5$ and $\kappa = 1.5$. This fact is important for understanding the mechanism of first order phase transitions.

The temperature anomalies of colloid water-containing systems, discovered by Drost-Hansen (1976) and studied by Etzler and coauthors (1987; 1991) occurred near 14-16^0; 29-32^0; 44-46^0 and 59-62^0C. At these temperatures the extrema of viscosity, disjoining pressure and molar excess entropy of water between quartz plates even with a separation 300-500 Å has been observed. These temperatures are close to predicted by our theory for bulk water anomalies, corresponding to integer values of $[\kappa]$ (see 5.7). Some deviations can be a result of interfacial water perturbations, induced by colloid particles and plates. It is a first theory which looks to be able to predict and explain the existence of Drost-Hansen temperatures.

The dimensions, concentration and stability of water clusters (primary librational effectons) in the volume of vicinal water should be bigger than that in bulk water due to their less mobility and to longer waves B length.

Interesting ideas, concerning the role of water clusters in biosystems were developed in works of John Watterson (1988a,b).

It was revealed in our laboratory (Kaivarainen, 1985; Kaivarainen et al., 1993) that nonmonotonic changes of water near Drost-Hansen temperatures are accompanied by in-phase change of different protein large-scale dynamics, related to their functioning. The further investigations of like phenomena are very important for understanding the molecular mechanisms of thermoadaptation of living organisms.

5.3. Physiological temperature and the least action principle

The Fig.5 a, b shows the resulting contributions to the total kinetic energy of water of two main subsystems: effectons and deformons. The minimum of deformons contribution at 43^0 is close to the physiological temperatures for warm-blooded animals.

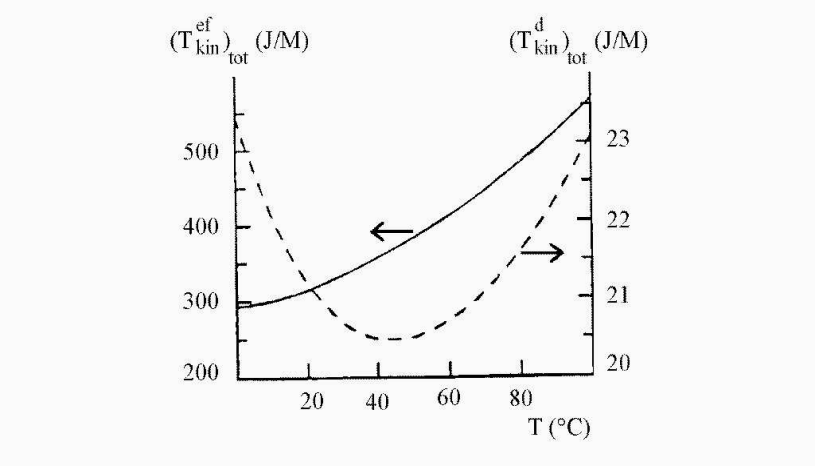

Fig. 5. Temperature dependences of two resulting contributions - effectons ($T^{ef}_{\rm kin}$) and deformons ($T^{d}_{\rm kin}$) of all types to the total kinetic energy of water.

The minima at temperature dependences of different contributions to the total kinetic energy of water at Fig.5 correspond to the best implementation of the *least action principle* in the form of Mopertui-Lagrange.

In such a form, this principle is valid for the conservative holonom systems, where limitations exist **for the displacements of the particles of this system, rather than the magnitudes of their velocities.** It states that among all the kinematically possible displacements of a system from one configuration to another, without changing total system energy, such a displacements are most probable for which the action (W) is least: $\Delta W = 0$. Here Δ is the symbol of total variation in coordinates, velocities and time.

The action is a fundamental physical parameter which has the dimension of the product of energy and time characterizing the dynamics of a system.

According to Hamilton, the action:

$$S = \int_{t_0}^{t} L dt \tag{5.8}$$

is expressed through the Lagrange function:

$$L = T_{\rm kin} - V, \tag{5.9}$$

where $T_{\rm kin}$ and V are the kinetic and potential energies of a system or a subsystem.

According to Lagrange, the action (W) can be expressed as:

$$W = \int_{t_0}^{t} 2T_{\rm kin} dt \tag{5.10}$$

We can assume that at the same integration limit the minimum value of the action $\Delta W \simeq 0$ corresponds to the minimum value of T_{kin}.. Then it can be said that at temperature about 43^0 the subsystems of deformons is most stable (see Fig. 6). This means that the equilibrium between the acoustic and optic states of primary and secondary effectons should be most stable at this temperature.

5.4. Mechanism of the 1st and 2nd order phase transitions in terms of the hierarchic theory

The abrupt increase of the total internal energy (U) as a result of ice melting (Fig. 6a), equal to $6.27kJ/M$, calculated from our theory is close to the experimental data ($6kJ/M$) (*Eisenberg*, 1969). The resulting thermoaccessibility (Z) during [ice → water] transition decreases abruptly, while potential and kinetic energies increase (Fig. 6b).

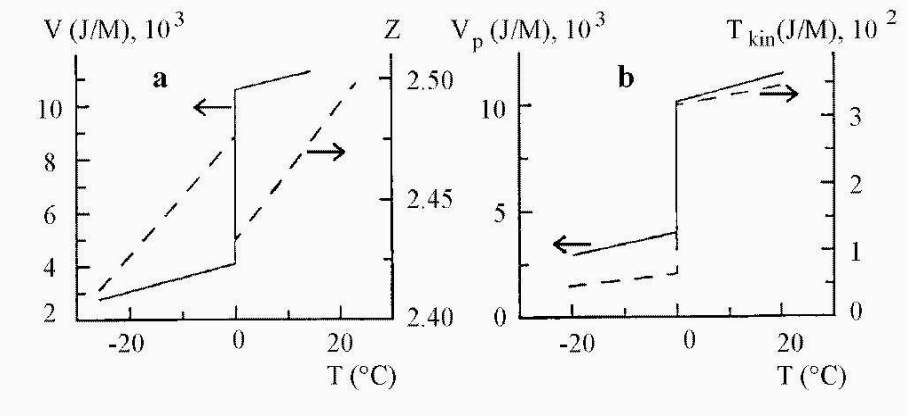

Fig. 6. The total internal energy ($U = T_{\rm kin} + V_p$) change during ice-water phase transition and change of the resulting thermoaccessibility (Z) - (a); changes in kinetic ($T_{\rm kin}$) and potential (V_p) energies (b) as a result of the same transition.

It is important that at the melting point H_2O molecules number in a *primary translational effecton* $(n_M^{tr})_{ef}$ decreases from 1 to $\simeq 0.4$ (Fig. 7a). It means that *the volume of this quasiparticle type gets smaller than the volume occupied by H_2O molecule.* According to our model, under such conditions the individual water molecules get the independent translation mobility. The number of water molecules forming a *primary libration effecton* decreases abruptly from about 3000 to 280, as a result of melting. The number of H_2O in the secondary librational effecton decreases correspondingly from ~ 1.25 to 0.5 (Fig. 7b).

Fig. $8a, b$ contains more detailed information on changes in primary librational effecton parameters in the course of ice melting.

The theoretical dependences obtained allow us to give a clear interpretation of the first order phase transitions. The condition of melting at $T = T_{cr}$ is realized in the course of heating when the number of molecules in the volume of primary translational effectons n_M decreases:

$$n_M^{tr} \geq 1 (T \leq T_{cr}) \stackrel{T_c}{\rightarrow} n_M^{tr} \leq 1 (T \geq T_{cr}) \tag{5.11}$$

Number of molecules $n_M^{tr,lb}$ in primary translational and librational effectons may be calculated using (4.63 a,b):

$$n_M^{tr,lb} = \left(V_{ef}^{tr,lb}/v_m\right) = \left[(1/n_{ef}^{tr,lb})/(V_0/N_A)\right]^{1/3} \tag{5.11a}$$

where: $(1/n_{ef}^{tr,lb})$ is the volume of primary translational or librational effecton; (V_0/N_A) is the volume, occupied by one molecule in condensed matter.

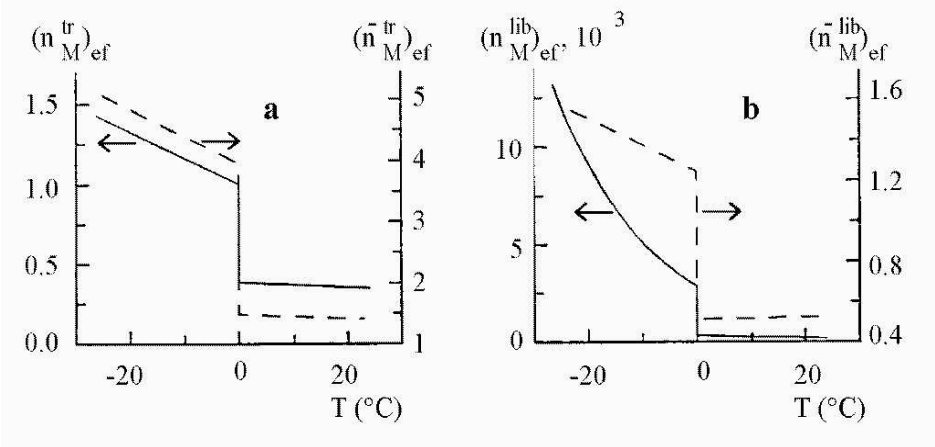

Fig. 7. Changes of the number of H_2O molecules forming primary $(n_M^{tr})_{ef}$ and secondary $(\bar{n}_M^{tr})_{ef}$ translational effectons during ice-water phase transition (a). Changes in the number of H_2O molecules forming primary $(n_M^{lb})_{ef}$ and secondary $(\bar{n}_M^{lb})_{ef}$ librational effectons (b) as a result of phase transitions.

The process of boiling, i.e. [liquid → gas] transition, as seen from Fig. 7a, is also determined by condition (5.11), but at this case it is realized for primary *librational* effectons.

This means that [gas → liquid] transition is related to origination (condensation) of the *primary librational effectons* which contain more than one molecule of substance.

In a liquid as compared to gas, the quantity of rotational degrees of freedom is decreased due to librational coherent effectons formation, but the number of translational degrees of freedom remains the same.

The translational degrees of freedom, in turn, also decreases, however, during [liquid → solid] phase transition, when the wave B length of molecules corresponding to their translations begins to exceed the mean distances between the centers of molecules (Fig. 7a). This process is accompanied by partial Bose-condensation of translational waves B and by the formation of coherent primary translational effectons, including more than one molecule. The size of librational effectons grows up abruptly during [*water* → *ice*] transition.

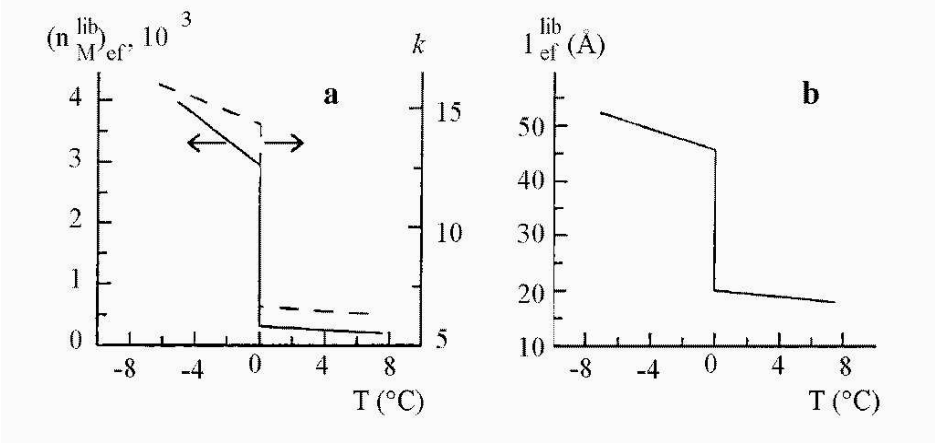

Fig. 8. Changes of the number of H_2O molecules forming a primary librational effecton $(n_M^{lb})_{ef}$, the number of H_2O molecules (κ) in the edge of this effecton (a) and the length of the effecton edge: $l_{ef}^{lb} = \kappa(V_0/N_0)^{1/3}$ (b) during the ice-water phase transition.

The enlarged primary librational effectons and librational polyeffectons, originating from the effectons "side-to-side" assembly due to Josephson' junctions, may serve as a centers of crystallization, necessary for $[liquid \rightarrow solid]$ transition. We assume here that probability of mesoscopic Bose condensation (BC) of molecules, involved in translations, as a condition of [liquid-solid] transition, increases in vicinity of crystallization centers, stimulated by interfacial effects.

The process of polyeffectons formation in very pure water is slow due to relatively low probability of their collision, necessary for primary effectons assembly. Such mechanism may be responsible for getting the supercooled water, i.e. liquid water, existing few degrees below 0^0C. The presence of impurities in form of colloid particles in water - stimulates the enlargement of librational effectons and their assembly, increasing in such a way the temperature of $[water \rightarrow ice]$ phase transition and making it closer to 0^0C. The opposite sharp transition of pure $[ice \rightarrow water]$, however, occur always at 0^0C at normal pressure of 1 atm. We may explain this phenomenon because the unified system of primary [translational + librational BC] of ice is more cooperative than the system of only librational BC of water. Consequently, the reaction of ice to temperature is more sensitive, than that of water and phase transition $[ice \rightarrow water]$ is more sharp, than $[water \rightarrow ice]$.

In contrast to first order phase transitions, the 2nd order phase transitions are not related to the abrupt change of primary effectons volume and concentration, **but only to their stability, related to their** $(a \rightleftharpoons b)^{1,2,3}_{tr,lb}$ **equilibrium shift, symmetry changes and polymerization.** Such phenomena may be a result of a gradual [temperature/pressure] - dependent decrease in the difference between the energy of a_i and b_i states of one of three standing waves B, forming primary effectons $\left[\ h\nu_p = h\left(\ \nu_b - \nu_a\ \right)\ \right]^i_{tr,lb}$. Such effect, registered by IR spectroscopy, is known as a soft mode low-frequency shift:

$$\left.\begin{array}{r} \left[\ h\nu_p = h\left(\ \nu_b - \nu_a\ \right)\ \right]^i_{tr,lb} \to\ 0 \\ \text{at}\ \left[\ \lambda^{T_c}_b = \lambda^{T_c}_a\ \right]^i_{tr,lb} > \left(\ V_0/N_0\ \right)^{1/3} \end{array}\right\} \tag{5.12}$$

The non-monotonic changes of sound velocity and the low-frequency shift of translational and librational bands in oscillatory spectra, according to our theory, should be followed by jump of heat capacity, compressibility and coefficient of thermal expansion. The parameters of elementary cells, *depending on geometry, stability and dynamics of primary effectons* are changing also. All these predictions of our theory are in accordance with experimental data.

Consequently, theory propose a new clear mechanism of 1st and 2nd order phase transitions. The number of molecules in the volume of primary effectons (5.11a) may be considered as a parameter of order for **1st order** phase transition.

The value of the constant of $(a \rightleftharpoons b)^{1,2,3}_{tr,lb}$ equilibrium

$$K_{(a\rightleftharpoons b)^{1,2,3}_{tr,lb}} = [a]/[b]^{1,2,3}_{tr,lb} = [h\nu_a/h\nu_b]^{1,2,3}_{tr,lb}$$

may serve as the parameter of order for **2nd order** phase transition.

The critical values of both parameters of order are close to one

5.5. The energy of quasiparticle discrete states. Activation energy of dynamics in water

Over the entire temperature range for water and ice, excluding conditions of 2nd order phase transitions, the energies of "acoustic" a-states of primary effectons (translational and librational ones) are lower than the energies of "optic" b-states (Fig.9). The energy of an ideal effecton (3RT) has the intermediate values.

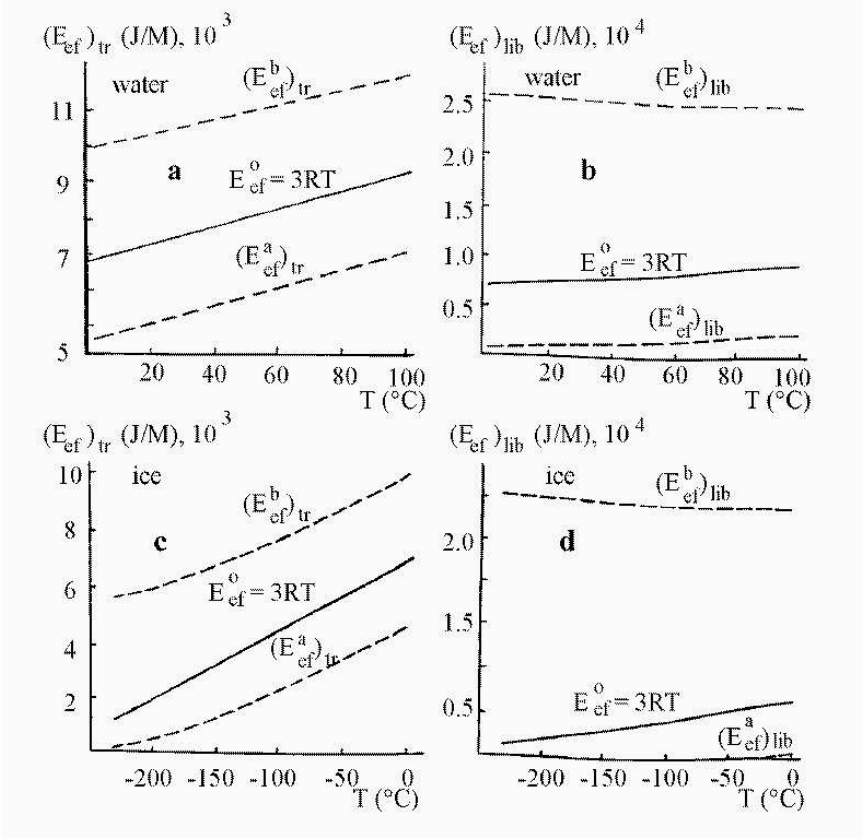

Fig. 9. Temperature dependences for the energy of primary effectons in "acoustic" (a) and "optical" (b) states and that for the energy of a harmonic 3D oscillator (the ideal thermal effecton: $E_0 = 3RT$) for water and ice calculated according to the formulae (4.6, 4.7 and 4.12): a) for primary translational effectons of water in a and b states; b) for primary librational effectons of water in a and b states; c) for primary translational effectons of ice in a and b states; d) for primary librational effectons of ice in a and b states.

According to the eq.(4.10 and 4.11) the *thermoaccessibility* of (a) and (b) states is determined by the absolute value of the difference:

$$\mid E^a_{ef} - 3kT \mid_{tr,lb}; \quad \mid E^b_{ef} - 3kT \mid_{tr,lb} .$$

where $E_0 = 3kT = 3h\nu_0$ is energy of an ideal effecton.

The ($a \Leftrightarrow b$) transitions (quantum beats) can be considered as autooscillations of quasiparticles around the thermal equilibrium state (E_0), which is quantum - mechanically prohibited. In terms of synergetics, the primary effectons are the medium active elements.

($b \rightarrow a$) transitions are related to origination of photons, and electromagnetic deformons, while the reverse ones ($a \rightarrow b$) correspond to absorption of them, i.e. annihilation of deformons.

The nonequilibrium conditions in the subsystems of effectons and deformons can be induced by the competition between discrete quantum and continuous heat energy distributions of different quasiparticles. Sometimes these nonequilibrium conditions could lead to macroscopic long-period oscillations in condensed matter.

The temperature dependences of the excitation (or fluctuation) energies for translational and librational macroeffectons in $A(a,\bar{a})$ and $B(b,\bar{b})$ states: $(\epsilon_M^A)_{tr,lb}$; $(\epsilon_M^B)_{tr,lb}$ and that for macrodeformons $(\epsilon_D^M)_{tr,lb}$ and superdeformons $(\epsilon_{D^*}^s)$, for water (a,b) and ice (c,d) can be calculated according to formulas (5.8, 5.9 and 5.10). $E_0 = 3RT$ is the energy of ideal quasiparticle, corresponding to thermal equilibrium energy.

The knowledge of the excitation energies of macrodeformons is important for calculation the viscosity and coefficient of self-diffusion (see sections 6.6 and 6.8).

The A and B states of macro- and supereffectons represent the significant deviations from thermal equilibrium. The transitions between these states termed: macro- and superdeformons represent the strong fluctuations of polarizabilities and, consequently, of refraction index and dielectric permeability.

The excitation energies of A and B states of macroeffectons are determined as:

$$(\epsilon_M^A)_{tr,lb} = -RT\ln(P_{ef}^a P_{ef}^a)_{tr,lb} = -RT\ln(P_M^A)_{tr,lb} \tag{5.13}$$

$$(\epsilon_M^B)_{tr,lb} = -RT\ln(P_{ef}^b P_{ef}^b)_{tr,lb} = -RT\ln(P_M^B)_{tr,lb} \tag{5.14}$$

where P_{ef}^a and $\bar{P}_{ef}^a$ are the thermoaccessibilities of the $(a) - eq.\,(4.10)$ and $(\bar{a}) - eq.\,(4.18)$ - states of the primary and secondary effectons, correspondingly; P_{ef}^b and $\bar{P}_{ef}^b$ are the thermoaccessibilities of $(b) - eq.(4.11)$ and $(\bar{b}) - eq.(4.19)$ states.

The activation energy for superdeformons is:

$$\begin{aligned}\epsilon_{D^*}^s &= -RT\ln(P_D^s) = -RT[\ln(P_D^M)_{tr} + \ln(P_D^M)_{lb}] = \\ &= (\epsilon_D^M)_{tr} + (\epsilon_D^M)_l\end{aligned} \tag{5.15}$$

The value $(\epsilon_D^M)_{tr} \approx 11.7kJ/M \approx 2.8$ kcal/M characterizes the activation energy for *translational self-diffusion of water molecules*, and $(\epsilon_D^M)_{lb} \approx 31kJ/M \approx 7.4$ kcal/M - the activation energy for librational self-diffusion of H_2O. The latter value *is close to the energy of the hydrogen bond in water* (Eisenberg, 1969).

On the other hand,the biggest fluctuations-superdeformons are responsible for the process of cavitational fluctuations in liquids and the emergency of defects in solids. They determine vapor pressure and sublimation, as it will be shown in our work.

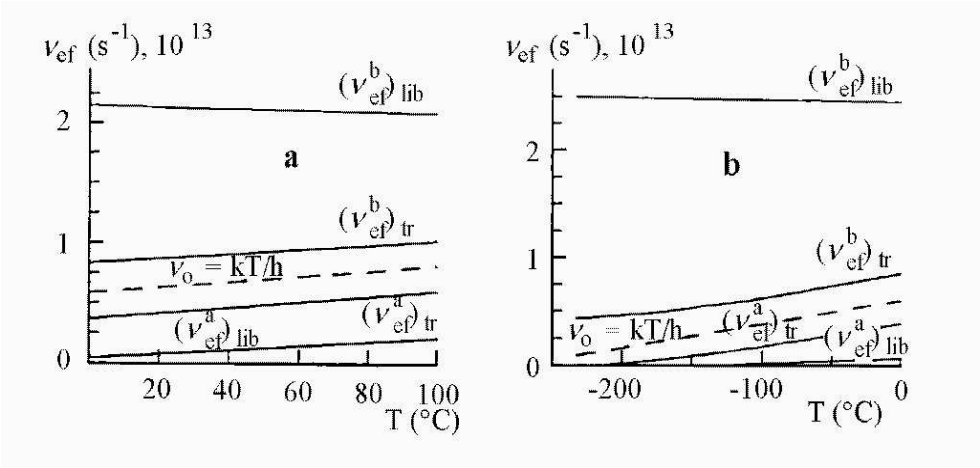

Fig. 10. Temperature dependences of the oscillation frequencies in (a) and (b) state of primary effectons - translational and librational for water (a) and ice (b), calculated from (Fig. 9).

The relative distribution of frequencies on Fig.10 is the same as of energies on Fig. 9. The values of these frequencies reflect the *minimum life-times* of corresponding states. The real life-time is dependent also on probability of "jump" from this state to another one and on probability of states excitation.

5.6. The life-time of quasiparticles and frequencies of their excitations

The set of formula, describing the dynamic properties of quasiparticles, introduced in mesoscopic theory was presented earlier.

For the case of $(a \Leftrightarrow b)^{1,2,3}$ transitions of primary and secondary effectons *(tr and lb),* their life-times in (a) and (b) states are the reciprocal value of corresponding frequencies: $[\tau_a = 1/\nu_a$ and $\tau_b = 1/\nu_b]^{1,2,3}_{tr,lb}$. These parameters and the resulting ones could be calculated from eqs.(2.27; 2.28) for primary effectons and (2.54; 2.55) for secondary ones.

The results of calculations, using eq.(4.56 and 4.57) for frequency of excitations of primary *tr and lb* effectons are plotted on Fig. 11a,b.

The frequencies of Macroconvertons and Superdeformons were calculated using eqs.(4.42 and 4.48).

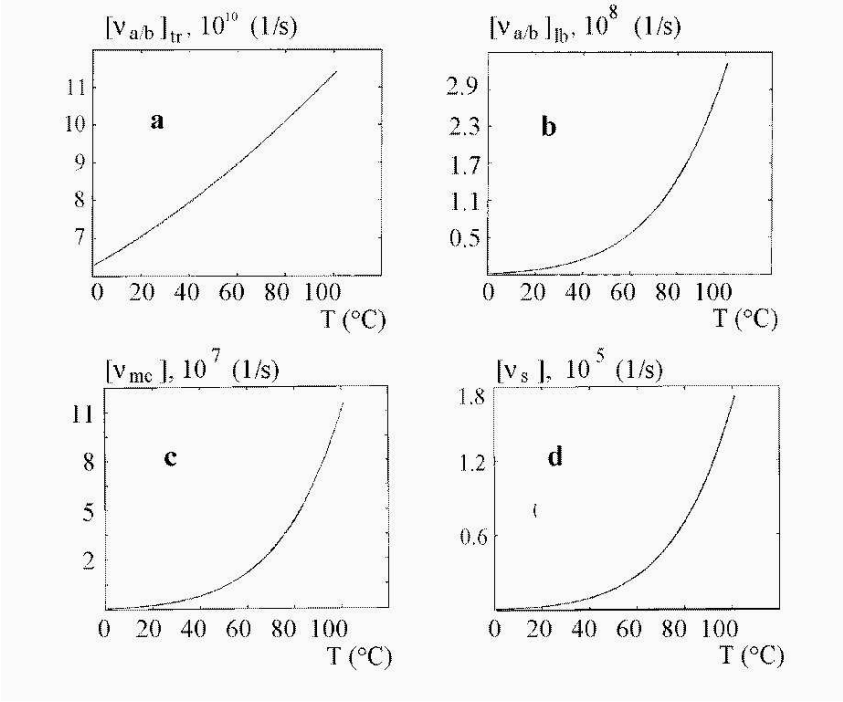

Fig. 11. (a) - Frequency of primary [tr] effectons excitations, calculated from eq.(4.56);

(b) - Frequency of primary [lb] effectons excitations, calculated from eq.(4.57);

(c) - Frequency of $[lb/tr]$ Macroconvertons (flickering clusters) excitations, calculated from eq.(4.42);

(d) - Frequency of Superdeformons excitations, calculated from eq.(4.48).

At the temperature interval $(0 - 100)^0C$ the frequencies of translational and librational macrodeformons (tr and lb) are in the interval of

$$(1.3 - 2.8) \cdot 10^9 s^{-1} \quad and \quad (0.2 - 13) \cdot 10^6 s^{-1} \tag{5.16}$$

correspondingly. The frequencies of (ac) and (bc) convertons could be defined also using our software and formulae, presented at the end of Section IV.

The frequency of primary translational effectons $[a \Leftrightarrow b]$ transitions at 20^0C, calculated from eq.(4.56) is

$$\nu \sim 7 \cdot 10^{10} \ (1/s) \tag{5.17}$$

It corresponds to electromagnetic wave length in water with refraction index $(n = 1.33)$ of:

$$\lambda = (cn)/\nu \sim 6mm \tag{5.18}$$

For the other hand, there are a lot of evidence, that irradiation of very different biological systems with such coherent electromagnetic field exert great influences on their properties (Grundler and Keilman, 1983).

Between the dynamics/function of proteins, membranes, etc. and dynamics of their aqueous environment the strong interrelation exists.

The frequency of macroconvertons, representing big density fluctuation in the volume of primary librational effecton at 37^0C is about $10^7(1/s)$ (Fig 11c), the frequency of librational macrodeformons at the same temperature is about 10^6 s^{-1},i.e. coincides **with frequency of large-scale protein cavities pulsations between open and closed to water states** (see Fig.11). *This confirm our hypothesis that the clusterphilic interaction is responsible for stabilization of the proteins cavities open state and that transition from the open state to the closed one is induced by coherent water cluster dissociation.*

The frequency of Superdeformons excitation (Fig.11d) is much lower:

$$\nu_s \sim (10^4 - 10^5)\ s^{-1} \tag{5.19}$$

Superdeformons are responsible for cavitational fluctuations in liquids and origination of defects in solids. Dissociation of oligomeric proteins, like hemoglobin or disassembly of actin and microtubules could be also related with such big fluctuations. Superdeformons could stimulate also the reversible dissociation of water molecules, which determines the pH value

$$H_2O \rightleftharpoons HO^- + H^+ \tag{5.20}$$

Recombination of HO^- and H^+ may be accompanied by emission of UV and visible photons. Corresponding radiation could be responsible for fraction of so-called biophotons.

The parameters, characterizing an average spatial distribution of primary lb and tr effectons in the bulk water are presented on the next Fig.12.

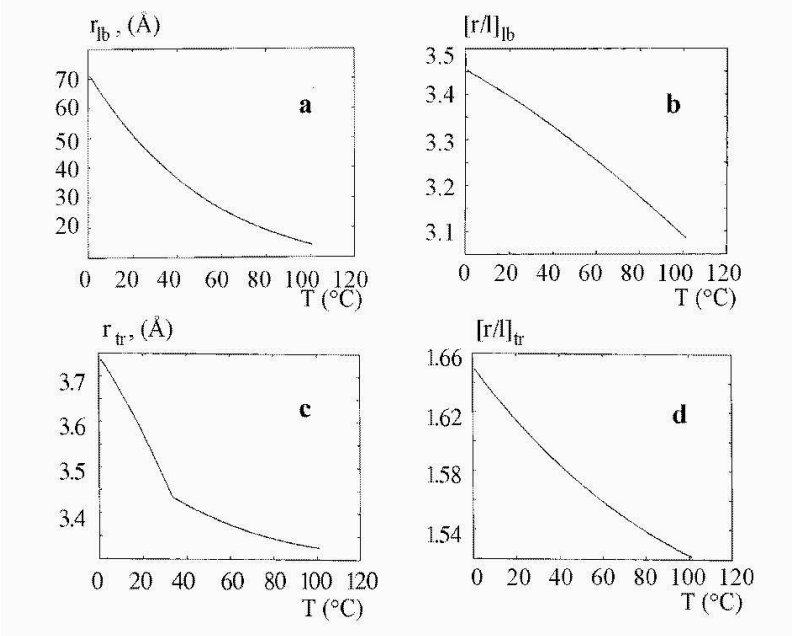

Fig. 12. Theoretical temperature dependencies of:

(a) - the space between centers of primary [lb] effectons (calculated in accordance to eq.4.62);

(b) - the ratio of space between primary [lb] effectons to their length (calculated, using eq.4.63);

(c) - the space between centers of primary [tr] effectons (in accordance to eq.4.62);

(d) - the ratio of space between primary [tr] effectons to their length (eq.4.63).

One can see from the Fig.12 that the dimensions of primary translational effectons are much smaller and concentration much higher than that of primary librational effectons. We have to keep in mind that these are the averaged spatial distributions of collective excitations. The formation of **polyeffectons** - coherent clusters of lb (in liquids) and tr (in solids) primary effectons, interacting side-by-side due to Josephson effect is possible also.

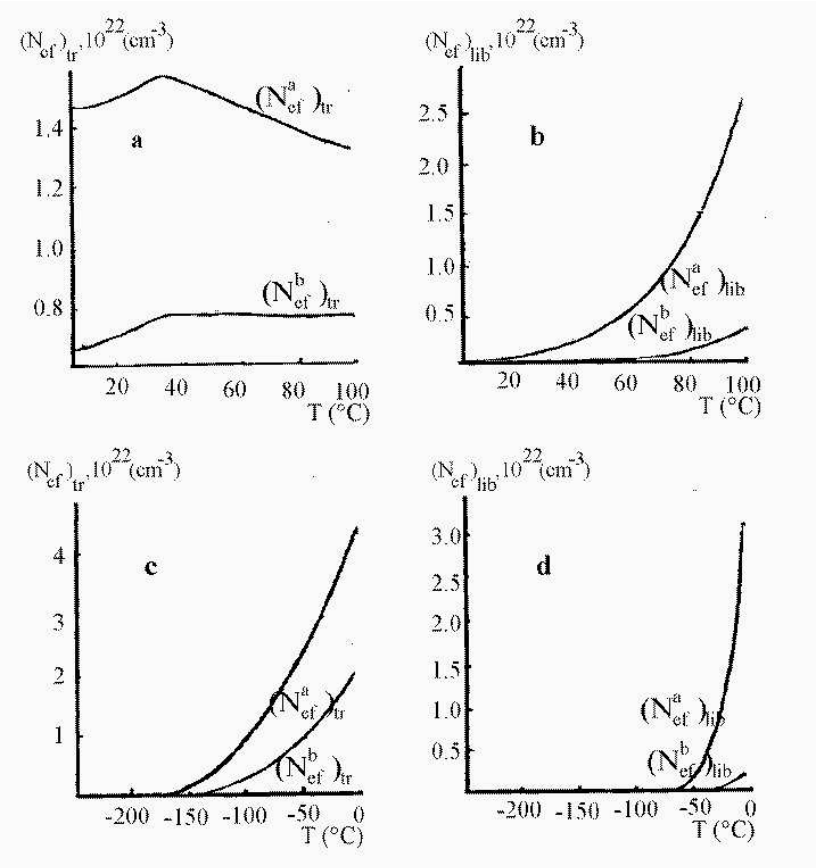

Fig. 13. Temperature dependences for the concentrations of primary effectons (translational and librational) in (a) and (b) states: $(N^a_{ef})_{tr,lb}$, $(N^b_{ef})_{tr,lb}$ for water (**a** and **b**); the similar dependencies for ice (**c** and **d**). Concentrations of quasiparticles were calculated from eqs.: $(N^a_{ef})_{tr,lb} = (n_{ef}P^a_{ef}/Z)_{tr,lb}$; $(N^b_{ef})_{tr,lb} = (n_{ef}P^b_{ef}/Z)_{tr,lb}$

These dependences can be considered as the quasiparticles distribution functions.

To get such information using conventional tools, i.e. by means of x-ray or neutron scattering methods is very complicated task. However, even in this case the final information about properties of collective excitations will not be so comprehensive as it leads from our theory.

The results, presented above, confirms the correctness of our model for liquids and solids, as a hierarchic system of 3D standing waves of different nature. It will be demonstrated below that application of Hierarchic theory could be useful for elucidation and quantitative analysis of very different physical properties.

6. INTERRELATION BETWEEN MESOSCOPIC AND MACROSCOPIC PARAMETERS OF MATTER

6.1. The state equation for real gas

The Clapeyrone-Mendeleyev equation sets the relationship between pressure (P), volume (V) and temperature (T) values for the ideal gas containing N_0 molecules (one mole):

$$PV = N_0 kT = RT \tag{6.1}$$

In the real gases interactions between the molecules and their sizes should be taken into account. It can be achieved by entering the corresponding amendments into the left part, to the right or to the both parts of eq. (1).

It was Van der Waals who choosed the first way more than a hundred years ago and derived the equation:

$$\left(P + \frac{a}{V^2}\right)\left(\ V - b\ \right) = RT \tag{6.2}$$

where the attraction forces are accounted for by the amending term (a/V^2), while the repulsion forces and the effects of the excluded volume accounted for the term (b).

Equation (2) correctly describes changes in P,V and T related to liquid-gas transitions on the qualitative level. However, the quantitative analysis by means of (2) is approximate and needs the fitting parameters. The parameters (a) and (b) are not constant for the given substance and depend on temperature. Hence, the Van der Waals equation is only some approximation describing the state of a real gas.

We propose a way to modify the right part of eq.(1), substituting it for the part of the kinetic energy (T) of 1 mole of the substance (eq.4.31 in [1, 2]) in real gas phase formed only by secondary effectons and deformons with nonzero impulse, affecting the pressure:

$$PV = \frac{2}{3}\bar{T}_{\text{kin}} = \frac{2}{3}V_0\frac{1}{Z}\sum_{tr,lb}\left[\bar{n}_{ef}\frac{\sum_1^3\left(\bar{E}^a_{1,2,3}\right)^2}{2m\left(\overline{v}^a_{ph}\right)^2}\left(\bar{P}^a_{ef}+\bar{P}^b_{ef}\right)+\right.$$

$$\left.+\,\bar{n}_d\frac{\sum_1^3\left(\bar{E}_d^{1,2,3}\right)^2}{2m\left(v_s\right)^2}\bar{P}_d\right]_{tr,lb} \tag{6.3}$$

The contribution to pressure caused by primary quasiparticles as Bose-condensate with the zero resulting impulse is equal to zero also.

It is assumed when using such approach that for real gases the model of a system of weakly interacted oscillator pairs is valid. The validity of such an approach for water is confirmed by available experimental data indicating the presence of dimers, trimers and larger H_2O clusters in the water vapor (Eisenberg and Kauzmann, 1975).

Water vapor has an intensive band in oscillatory spectra at $\tilde{\nu} = 200cm^{-1}$. Possibly, it is this band that characterizes the frequencies of quantum beats between "acoustic" (a) and "optic" (b) translational oscillations in pairs of molecules and small clusters. The frequencies of librational collective modes in vapor are absent.

The energies of primary gas quasiparticles ($h\nu_a$ and $h\nu_b$) can be calculated on the basis of the formulae used for a liquid (see section...).

However, to calculate the energies of secondary quasiparticles in ($\bar{\text{a}}$) and ($\bar{\text{b}}$) states the Bose-Einstein distribution must be used for the case when the temperature is higher than the Bose-condensation temperature ($T > T_0$) and the chemical potential is not equal to zero ($\mu < 0$). According to this distribution:

$$\left\{\bar{E}^a = h\bar{\nu}^a = \frac{h\nu^a}{\exp\left(\frac{h\nu^a-\mu}{kT}\right)-1}\right\}_{tr,lb}$$
$$\left\{\bar{E}^b = h\bar{\nu}^b = \frac{h\nu^b}{\exp\left(\frac{h\nu^b-\mu}{kT}\right)-1}\right\}_{tr,lb} \tag{6.4}$$

The kinetic energies of effectons $(\bar{a})_{tr,lb}$ and $(\bar{b})_{tr,lb}$ states are equal, only the potential energies differ as in the case of condensed matter.

All other parameters in basic equation (6.3) can be calculated as previously described.

6.2. New state equation for condensed matter

Using our eq.(4.3 from [1,2]) for the total internal energy of condensed matter (U_{tot}), we can present state equation in a more general form than (3).

For this end we introduce the notions of *internal pressure* (P_{in}), including **all type of interactions** between particles of matter and excluded molar volume (V_{exc}):

$$V_{\rm exc} = \frac{4}{3}\pi\alpha^* N_0 = V_0\left(\frac{n^2-1}{n^2}\right) \tag{6.5}$$

where α^* is the acting polarizability of molecules in condensed matter (see section...);

N_0 is Avogadro number, and V_0 is molar volume.

The general state equation can be expressed in the following form:

$$P_{\rm tot}V_{fr} = (P_{\rm ext} + P_{\rm in})(V_0 - V_{\rm exc}) = U_{ef} \tag{6.6}$$

where: $U_{ef} = U_{\rm tot}(1 + V/T^t_{\rm kin}) = U^2_{\rm tot}/T_{\rm kin}$ is the effective internal energy and:

$$(1 + V/T_{\rm kin}) = U_{\rm tot}/T_{\rm kin} = S^{-1}$$

is the reciprocal value of the total structural factor (*eq.*2.46*a of* [1]); $P_{\rm tot} = P_{\rm ext} + P_{\rm in}$ is total pressure, $P_{\rm ext}$ and $P_{\rm in}$ are external and internal pressures; $V_{fr} = V_0 - V_{\rm exc} = V_0/n^2$ (see eq.5) is a free molar volume; $U_{\rm tot} = V + T_{\rm kin}$ is the total internal energy, V and $T_{\rm kin}$ are total potential and kinetic energies of one mole of matter.

For the limit case of ideal gas, when $P_{\rm in} = 0$; $V_{\rm exc} = 0$; and the potential energy $V = 0$, we get from (6) the Clapeyrone - Mendeleyev equation (see 1):

$$P_{\rm ext}V_0 = T_{\rm kin} = RT$$

One can use equation of state (6) for estimation of sum of *all types of internal matter interactions*, which determines the internal pressure $P_{\rm in}$:

$$P_{\rm in} = \frac{U_{ef}}{V_{fr}} - P_{\rm ext} = \frac{n^2U^2_{\rm tot}}{V_0T_{\rm kin}} - P_{\rm ext} \tag{6.7}$$

where: the molar free volume: $V_{fr} = V_0 - V_{\rm exc} = V_0/n^2$;

and the effective total energy: $U_{ef} = U^2_{\rm tot}/T_{\rm kin} = U_{\rm tot}/{\rm S}$.

For solids and most of liquids with a good approximation: $P_{\rm in} \gg [P_{\rm ext} \sim 1$ atm. $= 10^5 Pa]$. Then from (7) we have:

$$P_{\rm in} \cong \frac{n^2U_{\rm tot}}{V_0S} = \frac{n^2}{V_0}\cdot U_{\rm tot}\left(1 + \frac{V}{T_{\rm kin}}\right) \tag{6.8}$$

where $S = T_{\rm kin}/U_{\rm tot}$ is a total structural factor; $T_{\rm kin}$ and V are total kinetic and potential energies, respectively.

For example for 1 mole of water under standard conditions we obtain:

$V_{\rm exc} = 8.4cm^3; V_{fr} = 9.6cm^3;\ V_0 = V_{\rm exc} + V_{fr} = 18cm^3;$

$P_{\rm in} \cong 380000$ atm. $= 3.8\cdot 10^{10}Pa$ (1 atm. $=10^5 Pa$).

The parameters such as sound velocity, molar volume, and the positions of translational and librational bands in oscillatory spectra that determine U_{ef} (4.3) depend on external pressure and temperature.

The results of computer calculations of $P_{\rm in}$ $(eq.7)$ for ice and water are presented on Fig. 14 a,b.

Polarizability and, consequently, free volume (V_{fr}) and $P_{\rm in}$ in (6.6) depend on energy of external electromagnetic fields.

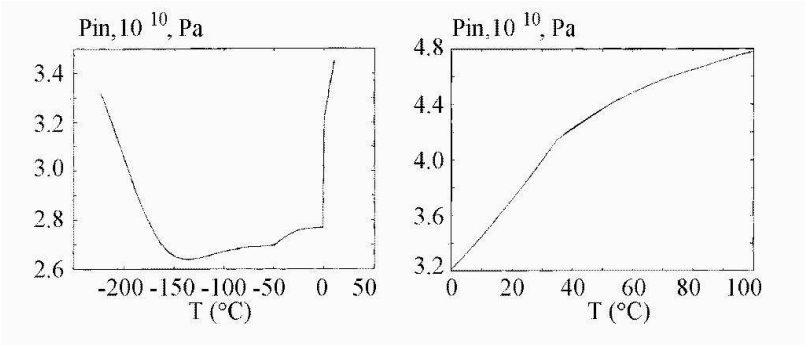

Fig. 14. (a) Theoretical temperature dependence of internal pressure ($P_{\rm in}$) in ice including the point of [ice $\Leftrightarrow$ water] phase transition; (b) Theoretical temperature dependence of internal pressure ($P_{\rm in}$) in water. Computer calculations were performed using eq. (6.7).

The minima of $P_{\rm in}(T)$ for ice at -140^0 and -50^0C in accordance with eq.(9) correspond to the most stable structure of this matter, related to temperature transition. In water some kind of transition appears at 35^0C, near physiological temperature.

There may exist conditions when the derivatives of internal pressure $\rm P_{in}$ are equal to zero:

$$(a): \left(\frac{\partial P_{\rm in}}{\partial P_{\rm ext}}\right)_T = 0 \quad \text{and} \quad (b): \left(\frac{\partial P_{\rm in}}{\partial T}\right)_{P_{\rm ext}} = 0 \tag{6.9}$$

This condition corresponds to the **minima of potential energy, i.e. to the most stable structure of given matter.** In a general case there may be a few metastable states when conditions (6.9) are fulfilled.

Equation of state (6.7) may be useful for the study of mechanical properties of condensed matter and their change under different influences.

Differentiation of (6.6) by external pressure gives us at T = *const:*

$$V_{fr} + \frac{\partial P_{fr}}{\partial P_{\rm ext}}(P_{\rm ex} + P_{\rm in}) + V_{fr}\frac{\partial P_{\rm in}}{\partial P_{\rm ext}} = \frac{\partial P_{ef}}{\partial P_{\rm ext}} \tag{6.10}$$

Dividing the left and right part of (6.10) by free volume V_{fr} we obtain:

$$\left(\frac{\partial P_{\rm in}}{\partial P_{\rm ext}}\right)_T = \left(\frac{\partial P_{ef}}{\partial P_{\rm ext}}\right)_T - \left[\ 1 + \beta_T(P_{\rm ext} + P_{\rm in})\ \right]_T \tag{6.11}$$

where: $\beta_T = -(\partial V_{fr}/\partial P_{\rm ext})/V_{fr}$ is isothermal compressibility. From (6.9) and (6.11) we derive condition for the *maximum stability* of matter structure:

$$\left(\frac{\partial P_{ef}}{\partial P_{\rm ext}}\right)_T = 1 + \beta_T^0 P_{\rm tot}^{\rm opt} \tag{6.12}$$

where: $P_{\rm tot}^{\rm opt} = P_{\rm ext} + P_{\rm in}^{\rm opt}$ is the "optimum" total pressure.

The derivative of (6.6) by temperature gives us at $P_{\rm ext} = const$:

$$P_{\rm tot}\left(\frac{\partial V_{fr}}{\partial T}\right)_{P_{\rm ext}} + V_{fr}\left(\frac{\partial P_{\rm in}}{\partial T}\right)_{P_{\rm ext}} = \left(\frac{\partial U_{ef}}{\partial T}\right)_{P_{\rm ext}} = C_V \tag{6.13}$$

where

$$\left(\frac{\partial V_{fr}}{\partial T}\right)_{P_{\rm ext}} = \left(\frac{\partial V_0}{\partial T}\right)_{P_{\rm ext}} - \frac{4}{3}\pi N_0 \left(\frac{\partial \alpha^*}{\partial T}\right)_{P_{\rm ext}} \tag{6.14}$$

and $$\left(\frac{\partial V_{\rm tot}}{\partial T}\right)_{P_{\rm ext}} = \frac{\partial P_{\rm in}}{\partial T} \tag{6.14a}$$

From our mesoscopic theory of refraction index (see section..) the acting polarizability α^* is:

$$\alpha^* = \frac{\left(\frac{n^2-1}{n^2}\right)}{\frac{4}{3}\pi\frac{N_0}{V_0}} \tag{6.15}$$

When condition (6.9b) is fulfilled, we obtain for optimum internal pressure ($P_{\rm in}^{\rm opt}$) from (6.13):

$$P_{\rm in}^{\rm opt} = C_V / \left(\frac{\partial V_{fr}}{\partial T}\right)_{P_{\rm ext}} - P_{\rm ext} \tag{6.16}$$

or

$$P_{\rm in}^{\rm opt} = \frac{C}{V_{fr}\gamma} - P_{\rm ext}, \tag{6.17}$$

where

$$\gamma = (\partial V_{fr}/\partial T)/V_{fr} \tag{6.18}$$

is the thermal expansion coefficient;

V_{fr} is the total free volume in 1 mole of condensed matter:

$$V_{fr} = V_0 - V_{\rm exc} = V_0/n^2 \tag{6.19}$$

It is taken into account in (6.13) and (6.19) that

$$(\partial V_{\text{exc}}/\partial T) \cong 0 \tag{6.20}$$

because, as has been shown by our computer simulations,

$$\partial \alpha^*/\partial T \cong 0$$

Dividing the left and right parts of (6.13) by $P_{\text{tot}} V_{fr} = U_{ef}$, we obtain for the heat expansion coefficient:

$$\gamma = \frac{C_V}{U_{ef}} - \frac{1}{P_{\text{tot}}} \left(\frac{\partial P_{\text{in}}}{\partial T} \right)_{P_{\text{ext}}} \tag{6.21}$$

Under metastable states, when condition (6.9 b) is fulfilled,

$$\gamma^0 = C_V/U_{ef} \tag{6.22}$$

Putting (6.8) into (6.12), we obtain for isothermal compressibility of metastable states corresponding to (6.9a) following formula:

$$\beta_T^0 = \frac{V_0 T_{\text{kin}}}{n^2 U_{\text{tot}}^2} \left(\frac{\partial U_{ef}}{\partial P_{\text{ext}}} - 1 \right) \tag{6.23}$$

It seems that our equation of state (6.7) may be used to study different types of external influences (pressure, temperature, electromagnetic radiation, deformation, etc.) on the thermodynamic and mechanic properties of solids and liquids.

6.3. Vapor pressure

When a liquid is incubated long enough in a closed vessel at constant temperature, then an equilibrium between the liquid and vapor is attained.

At this moment, the number of molecules evaporated and condensed back to liquid is equal. The same is true of the process of sublimation.

There is still no satisfactory quantitative theory for *vapor pressure* calculation.

We can suggest such a theory using our notion of *superdeformons*, representing the biggest thermal fluctuations (see Table 1 and Introduction). The basic idea is that the external equilibrium vapor pressure is related to internal one (P_{in}^S) with coefficient determined by the probability of cavitational fluctuations (superdeformons) in the **surface layer** of liquids or solids.

In other words due to excitation of superdeformons with probability (P_D^S), the internal pressure (P_{in}^S) in surface layers, determined by the total contributions of all intramolecular interactions turns to external one - vapor pressure (P_V). It is something like a compressed spring energy realization due to trigger switching off.

For taking into account the difference between the surface and bulk internal pressure ($P_{\rm in}$) we introduce the semi-empirical surface pressure factor (q^S) as:

$$P_{\rm in}^S = q^S P_{\rm in} - P_{\rm ext} = q^S \cdot \frac{n^2 U_{\rm tot}}{V_0 S} - P_{\rm ext} \tag{6.24}$$

where: $\rm P_{in}$ corresponds to *eq.*(7); $S = T_{\rm kin}/U_{\rm tot}$ is a total structure factor.

The value of surface factor (q^S) for liquid and solid states is not the same:

$$q_{\rm liq}^S < q_{\rm sol}^S \tag{6.25}$$

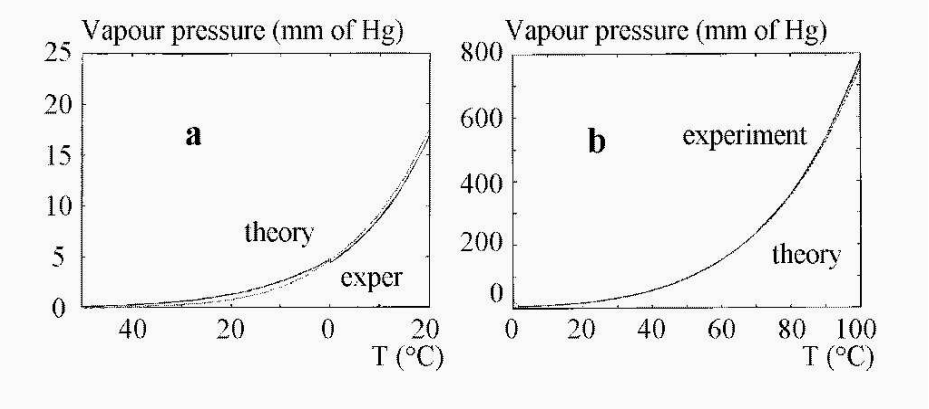

Fig. 15. a) Theoretical (−) and experimental (··) temperature dependences of vapor pressure ($P_{\rm vap}$) for ice (a) and water (b) including phase transition region. Computer calculations were performed using eq. (6.26).

Multiplying (6.24) to probability of superdeformons excitation we obtain for vapor pressure, resulting from evaporation or sublimation, the following formulae:

$$P_{vap} = P_{\rm in}^S \cdot P_D^S = \left(q^S \frac{n^2 U_{\rm tot}^2}{V_0 T_{\rm kin}} - P_{\rm ext} \right) \cdot \exp\left(-\frac{E_D^S}{kT} \right) \tag{6.26}$$

where:

$$P_D^S = \exp\left(-\frac{E_D^S}{kT} \right) \tag{6.27}$$

is a probability of superdeformons excitation (see eqs. 3.37, 3.32 and 3.33).

We can assume, that the difference in the surface and bulk internal pressure is determined mainly by difference in total internal energy ($U_{\rm tot}$) but not in kinetic one (T_k). Then a pressure surface factor could be presented as:

$$q^S = \gamma^2 = (U_{\rm in}/U_{\rm tot})^2$$

where: $\gamma = U^S_{\rm tot}/U_{\rm tot}$ is the **surface energy factor**, reflecting the ratio of surface and bulk total energy.

Theoretical calculated temperature dependences of vapor pressure, described by (6.26) coincide very well with experimental ones for water at $q^S_{\rm liq} = 3.1$ ($\gamma_l = 1.76$) and for ice at $q^S_{\rm sol} = 18$ ($\gamma_s = 4.24$) (Fig. 15).

The almost five-times difference between $q^S_{\rm sol}$ and $q^S_{\rm liq}$ means that the *surface* properties of ice differ from *bulk* ones much more than for liquid water.

The surface factors $q^S_{\rm liq}$ and $q^S_{\rm sol}$ should be considered as a fit parameters. The $q^S = \gamma^2$ is the only one fit parameter that was used in our hierarchic mesoscopic theory. Its calculation from the known vapor pressure or surface tension can give an important information itself.

6.4. Surface tension

The resulting surface tension is introduced in our mesoscopic model as a sum:

$$\sigma = (\sigma_{tr} + \sigma_{lb}) \tag{6.28}$$

where: σ_{tr} and σ_{lb} are translational and librational contributions to surface tension. Each of these components can be expressed using our mesoscopic state equation (6.7), taking into account the difference between surface and bulk total energies (q^S), introduced in previous section:

$$\sigma_{tr,} = \frac{1}{\frac{1}{\pi}(Vlb_{ef})^{2/3}_{tr,lb}} \left[\frac{q^S P_{\rm tot}(P_{ef}V_{ef})_{tr,lb} - P_{\rm tot}(P_{ef}V_{ef})_{tr,lb}}{(P_{ef}+P_t)_{tr} + (P_{ef}+P_t)_{lb} + (P_{\rm con}+P_{\rm cMt})} \right] \tag{6.29}$$

where $(V_{ef})_{tr,lb}$ are volumes of primary tr and lib effectons, related to their concentration $(n_{ef})_{tr,lb}$ as:

$$(V_{ef})_{tr,lb} = (1/n_{ef})_{tr,lb};$$

$$r_{tr,lb} = \frac{1}{\pi}(V_{ef})^{2/3}_{tr,lb}$$

is an effective radius of the primary translational and librational effectons, localized on the surface of condensed matter; q^S is the surface factor, equal to that used in eq.(6.24-6.26); $[P_{\rm tot} = P_{\rm in} + P_{\rm ext}]$ is a total pressure, corresponding to eq.(6.6); $(P_{ef})_{tr,lb}$ is a total probability of primary effecton excitations in the (a) and (b) states:

$$(P_{ef})_{tr} = (P^a_{ef} + P^b_{ef})_{tr}$$

$$(P_{ef})_{lb} = (P^a_{ef} + P^b_{ef})_{lb}$$

$(P_t)_{tr}$ and $(P_t)_{lb}$ in (29) are the probabilities of corresponding transiton excitation;

$P_{\rm con} = P_{ac} + P_{bc}$ is the sum of probabilities of $[a]$ and $[b]$ *convertons;* $P_{\rm cMt} = P_{ac}\, P_{bc}$ is a probability of Macroconvertons excitation (see Introduction).

The eq. (6.29) contains the ratio:

$$(V_{ef}/V^{2/3}_{ef})_{tr,lb} = l_{tr,lb} \tag{6.30}$$

where: $l_{tr} = (1/n_{ef})^{1/3}_{tr}$ and $l_{lb} = (1/n_{ef})^{1/3}_{\rm lib}$ are the length of the ribs of the primary translational and librational effectons, approximated by cube.

Using (6.30) and (6.29) the resulting surface tension (6.28) can be presented as:

$$\sigma = \sigma_{tr} + \sigma_{lb} = \pi \frac{P_{\rm tot}(q^S - 1) \cdot \left[\ (P_{ef})_{tr} l_{tr} + (P_{ef}) l_{lb}\ \right]}{(P_{ef} + P_t)_{tr} + (P_{ef} + P_t)_{lb} + (P_{\rm con} + P_{\rm cMt})} \tag{6.31}$$

where translational component of surface tension is:

$$\sigma_{tr} = \pi \frac{P_{\rm tot}(q^s - 1)(P_{ef})_{tr} l_{tr}}{(P_{ef} + P_t)_{tr} + (P_{ef} + P_t)_{lb} + (P_{\rm con} + P_{\rm cMt})} \tag{6.32}$$

and librational component of σ is:

$$\sigma_{lb} = \pi \frac{P_{\rm tot}(q^S - 1)(P_{ef})_{lb} l_{lb}}{(P_{ef} + P_t)_{lb} + (P_{ef} + P_t)_{lb} + (P_{\rm con} + P_{\rm cMt})} \tag{6.33}$$

Under the boiling condition when $q^S \to 1$ as a result of $(U^S_{\rm tot} \to U_{\rm tot})$, then σ_{tr}, σ_{lb} and σ tends to zero. The maximum depth of the surface layer, which determines the σ_{lb} is equal to the length of edge of cube (l_{lb}), that approximates the shape of primary **librational** effectons. It decreases from about 20 Å at 0^0C till about 2.5 Å at 100^0C (see Fig. 4b). Monotonic decrease of (l_{lb}) with temperature could be accompanied by nonmonotonic change of probabilities of [lb/tr] convertons and macroconvertons excitations (see comments to Fig 4a). Consequently, the temperature dependence of surface tension on temperature can display anomalies at definite temperatures. This consequence of our theory is confirmed experimentally (Adamson, 1982; Drost-Hansen and Lin Singleton, 1992).

The thickness of layer (l_{tr}), responsible for contribution of **translational** effectons in surface tension (σ_{tr}) has the dimension of one molecule in all temperature interval for liquid water.

The results of computer calculations of σ (eq.6.31) for water and experimental data are presented at Fig.16.

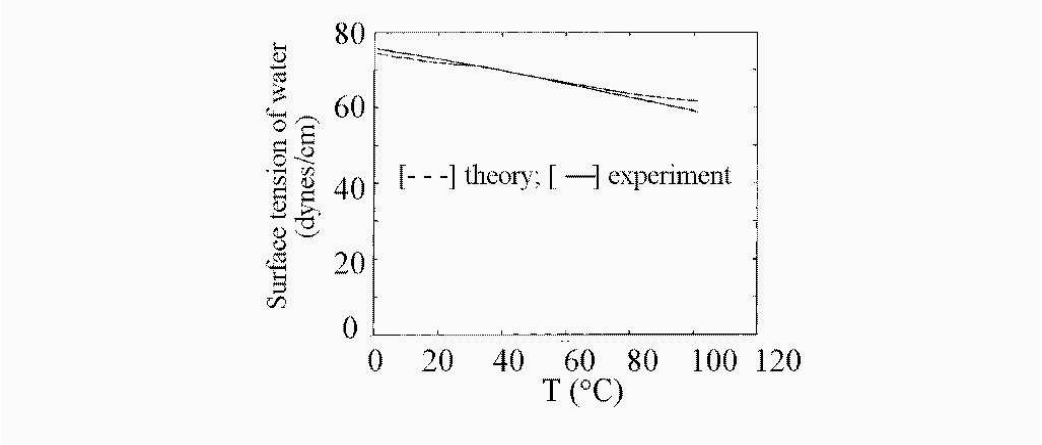

Fig. 16. Experimental (—) and theoretical (- - -) temperature dependences of the surface tension for water, calculated from eq.(6.31).

It is obvious, that the correspondence between theory and experiment is very good, confirming in such a way the correctness of our model and Hierarchic concept in general.

6.5. Mesoscopic theory of thermal conductivity

Thermal conductivity may be related to phonons, photons, free electrons, holes and [electron-hole] pairs movement.

We will discuss here only the main type of thermal conductivity in condensed matter, related to phonons.

The analogy with the known formula for thermal conductivity (κ) in the framework of the kinetic theory for gas is used:

$$\kappa = \frac{1}{3} C_v v_s \Lambda \tag{6.34}$$

where C_v is the heat capacity of condensed matter, v_s is sound velocity, characterizing the speed of phonon propagation in matter, and Λ is the average **length of free run** of phonons.

The value of Λ depends on the scattering and dissipation of phonons at other phonons and different types of defects. Usually decreasing temperature increases Λ.

Different factors influencing a thermal equilibrium in the system of phonons are discussed. Among them are the so called U- and N- processes describing the types of phonon-phonon interaction. However, the traditional theories are unable to calculate Λ directly.

Mesoscopic theory introduce two contributions to thermal conductivity: related to phonons, irradiated by secondary effectons and forming **secondary**

translational and librational deformons $(\kappa_{sd})_{tr,lb}$ and to phonons, irradiated by a and b convertons $[tr/lb]$, forming the convertons-induced deformons $(\kappa_{cd})_{ac.bc}$:

$$\kappa = (\kappa_{sd})_{tr,lb} + (\kappa_{cd})_{ac.bc} = \frac{1}{3} C_v v_s [(\Lambda_{sd})_{tr,lb} + (\Lambda_{cd})_{ac,bc}] \tag{6.35}$$

where: **free runs** of secondary phonons (tr and lb) are represented as:

$$1/(\Lambda_{sd})_{tr,lb} = 1/(\Lambda_{tr}) + 1/(\Lambda_{lb}) = (\overline{\nu}_d)_{tr}/v_s + (\overline{\nu}_d)_{lb}/v_s$$

consequently:

$$1/(\Lambda_{sd})_{tr,lb} = \frac{v_s}{(\overline{\nu}_d)_{tr} + (\overline{\nu}_d)_{lb}} \tag{6.36}$$

and free runs of convertons-induced phonons:

$$1/(\Lambda_{cd})_{ac,bc} = 1/(\Lambda_{ac}) + 1/(\Lambda_{bc}) = (\nu_{ac})/v_s + (\nu_{bc})/v_s$$

$$\text{consequently: } (\Lambda_{sd})_{tr,lb} = \frac{v_s}{(\nu_d)_{tr} + (\nu_d)_{lb}} \tag{6.37}$$

The heat capacity: $C_V = \partial U_{\text{tot}}/\partial T$ can be calculated also from our theory (see Chapter 4 and 5).

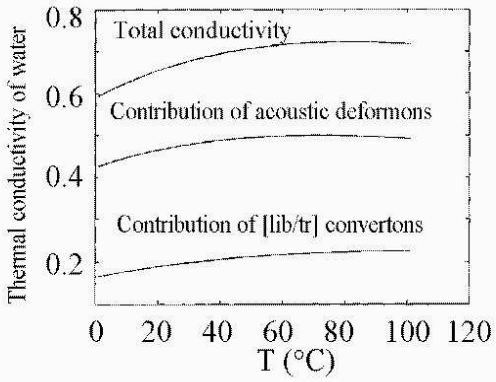

Fig. 17. Temperature dependences of total thermal conductivity for water and contributions, related to acoustic deformons and $[lb/tr]$convertons. The dependences were calculated, using eq. (37).

Quantitative calculations show that formula (6.35), based on our mesoscopic model, works well for water (Fig. 17). It could be used for any other condensed matter also if positions of translational and librational bands, sound velocity and molar volume for this matter at the same temperature interval are known.

The small difference between experimental and theoretical data can reflect the contributions of non-phonon process in thermal conductivity, related to macrodeformons, superdeformons and macroconvertons, i.e. big fluctuations.

6.6. Mesoscopic theory of viscosity for liquids and solids

The viscosity is determined by the energy dissipation as a result of medium (liquid or solid) structure deformation. Viscosity corresponding to the shift deformation is named *shear viscosity*. So- called *bulk viscosity* is related to deformation of volume parameters and corresponding dissipation. These types of viscosity have not the same values and nature.

The statistical theory of irreversible process leads to the following expression for shear viscosity (Prokhorov, 1988):

$$\eta = nkT\tau_p + (\mu_\infty - nkT)\tau_q \tag{6.38}$$

where $[n]$ is the concentration of particles, μ_∞ is the modulus of instant shift characterizing the instant elastic reaction of medium, τ_p and τ_q are the relaxation times of impulses and coordinates, respectively.

However, eq.(38) is inconvenient for practical purposes due to difficulties in determination of τ_p, τ_q and μ_∞.

Sometimes in a narrow temperature interval the empirical Ondrade equation is working:

$$\eta = A(T) \cdot \exp(\beta/T) \tag{6.39}$$

A(T) is a function poorly dependent on temperature.

A good results in study the microviscosity problem were obtained by combining the model of molecular rotational relaxation and the Kramers equation (Åkesson et al., 1991). However, the using of the fit parameters was necessarily in this case also.

We present here our mesoscopic theory of viscosity. To this end the dissipation processes, related to $(A \rightleftharpoons B)_{tr.lb}$ cycles of translational and librational macroeffectons and (a,b)-*convertons* excitations were used. The same approach was employed for elaboration of mesoscopic theory of diffusion in condensed matter (see next section).

In contrast to liquid state, the viscosity of solids is determined by the biggest fluctuations: **supereffectons** and **superdeformons**, resulting from simultaneous excitations of translational and librational macroeffectons and macrodeformons in the same volume.

The dissipation phenomena and ability of particles or molecules to diffusion are related to the local fluctuations of the free volume $(\Delta v_f)_{tr,lb}$. According to mesoscopic theory, the fluctuations of free volume and that of density occur in the almost macroscopic volumes of translational and librational macrodeformons and in mesoscopic volumes of **macroconvertons**, equal to volume of primary librational effecton at the given conditions. Translational and librational types of macroeffectons determine two types of viscosity, i.e. translational (η_{tr}) and librational (η_{lb}) ones. They can be attributed to the bulk viscosity. The contribution to viscosity, determined by *(a and b)- convertons is much more local and may be responsible for microviscosity and mesoviscosity.*

Let us start from calculation of the additional free volumes (Δv_f) originating from fluctuations of density, accompanied the translational and librational macrodeformons (macrotransitons).

For 1 mole of condensed matter the following ratio between free volume and concentration fluctuations is true:

$$\left(\frac{\Delta v_f}{v_f}\right)_{tr,lb} = \left(\frac{\Delta N_0}{N_0}\right)_{tr,lb} \tag{6.40}$$

where N_0 is the average number of molecules in 1 mole of matter

$$\text{and} \qquad (\Delta N_0)_{tr,lb} = N_0 \left(\frac{P_D^M}{Z}\right)_{tr,lb} \tag{6.41}$$

is the number of molecules changing their concentration as a result of translational and librational macrodeformons excitation.

The probability of translational and librational macroeffectons excitation (see eqs. 3.23; 3.24):

$$\left(\frac{P_D^M}{Z}\right)_{tr,lb} = \frac{1}{Z} \exp\left(-\frac{\epsilon_D^M}{kT}\right)_{tr,lb} \tag{6.42}$$

where Z is the total partition function of the system.

Putting (6.41) to (6.40) and dividing to Avogadro number (N_0), we obtain the fluctuating free volume, reduced to 1 molecule of matter:

$$\Delta v_f^0 = \frac{\Delta v_f}{N_0} = \left[\frac{v_f}{N_0}\left(\frac{P_D^M}{Z}\right)\right]_{tr,lb} \tag{6.43}$$

It has been shown above (eq.6.19) that the average value of free volume in 1 mole of matter is:

$$v_f = V_0/n^2$$

Consequently, for reduced fluctuating (additional) volume we have:

$$(\Delta v_f^0)_{tr,lb} = \frac{V_0}{N_0 n^2} \frac{1}{Z} \exp\left(-\frac{\epsilon_D^M}{kT}\right)_{tr,lb} \tag{6.44}$$

Taking into account the dimensions of viscosity and its physical sense, it should be proportional to the work (activation energy) of fluctuation-dissipation, necessary for creating the unit of additional free volume: $(E_D^M/\Delta v_f^0)$, and the period of $(A \rightleftharpoons B)_{tr.lb}$ cycles of translational and librational macroeffectons $\tau_{A\rightleftharpoons B}$, determined by the life-times of all intermediate states (eq.46).

In turn, the energy of dissipation should be strongly dependent on the structural factor (S): the ratio of kinetic energy of matter to its total internal energy. We postulate here that this dependence for viscosity is cubical: $(T_k/U_{\text{tot}})^3 = S^3$**.**

Consequently, the contributions of translational and librational macrodeformons to resulting viscosity we present in the following way:

$$\eta^{M}_{tr,lb} = \left[\frac{E^{M}_{D}}{\Delta v^{0}_{f}} \tau^{M} \left(\frac{T_k}{U_{\rm tot}} \right)^3 \right]_{tr,lb} \tag{6.45}$$

where: reduced fluctuating volume (Δv^{0}_{f}) corresponds to (44); the energy of macrodeformons: $[E^{M}_{D} = -kT\,(\ln P^{M}_{D})]_{tr,lb}$.

The cycle-periods of the *tr* and *lib* macroeffectons has been introduced as:

$$\left[\tau^{M} = \tau_A + \tau_B + \tau_D\right]_{tr,lb} \tag{6.46}$$

where: characteristic life-times of macroeffectons in A, B-states and that of transition state in the volume of primary electromagnetic deformons can be presented, correspondingly, as follows:

$$\left[\tau_A = (\tau_a\, \tau_{\overline{a}})^{1/2}\right]_{tr,lb} \quad \text{and} \quad \left[\tau_A = (\tau_a\, \tau_{\overline{a}})^{1/2}\right]_{tr,lb} \tag{6.47}$$

$$\left[\tau_D = |(1/\tau_A) - (1/\tau_B)|^{-1}\right]_{tr,lb}$$

Using (6.47, 6.46 and 6.44) it is possible to calculate the contributions of ($A \rightleftharpoons B$) cycles of translational and librational macroeffectons to viscosity separately, using (6.45).

The averaged contribution of Macroexcitations (tr and lb) in viscosity is:

$$\eta^{M} = \left[\ (\eta)^{M}_{tr}\,(\eta)^{M}_{lb}\ \right]^{1/2} \tag{6.48}$$

The contribution of *a* and *b convertons* to viscosity of liquids could be presented in a similar to (6.44-6.48) manner after substituting the parameters of *tr and lb* macroeffectons with parameters of *a and b* convertons:

$$\eta_{ac,bc} = \left[\frac{E_c}{\Delta v^{0}_{f}} \tau_c \left(\frac{T_k}{U_{\rm tot}} \right)^3 \right]_{ac,bc} \tag{6.49}$$

where: reduced fluctuating volume of (*a* and *b*) convertons $(\Delta v^{0}_{f})_{ac,bc}$ corresponds to:

$$(\Delta v^{0}_{f})_{ac,bc} = \frac{V_0}{N_0 n^2} \frac{1}{Z} P_{ac,bc} \tag{6.50}$$

where: P_{ac} and P_{bc} are the relative probabilities of *tr*/*lib* interconversions between *a* and *b* states of translational and librational primary effectons (see Introduction); E_{ac} and E_{bc} are the excitation energies of (*a* and *b*) convertons correspondingly (see section 4);

Characteristic life-times for ac-convertons and bc-convertons $[tr/lb]$ in the volume of primary librational effectons ("flickering clusters") could be presented as:

$$\begin{array}{l} \tau_{ac} = (\tau_a)_{tr} + (\tau_a)_{lb} = (1/\nu_a)_{tr} + (1/\nu_a)_{lb} \\ \tau_{bc} = (\tau_b)_{tr} + (\tau_b)_{lb} = (1/\nu_b)_{tr} + (1/\nu_b)_{lb} \end{array} \tag{6.51}$$

The averaged contribution of the both types of convertons in viscosity is:

$$\eta_c = (\eta_{ac}\, \eta_{bc})^{1/2} \tag{6.52}$$

This contribution could be responsible for microviscosity or better term: **meso-viscosity**, related to volumes, equal to that of primary librational effectons.

The resulting viscosity (Fig.18) is a sum of the averaged contributions of macrodeformons and convertons:

$$\eta = \eta^M + \eta_c \tag{6.53}$$

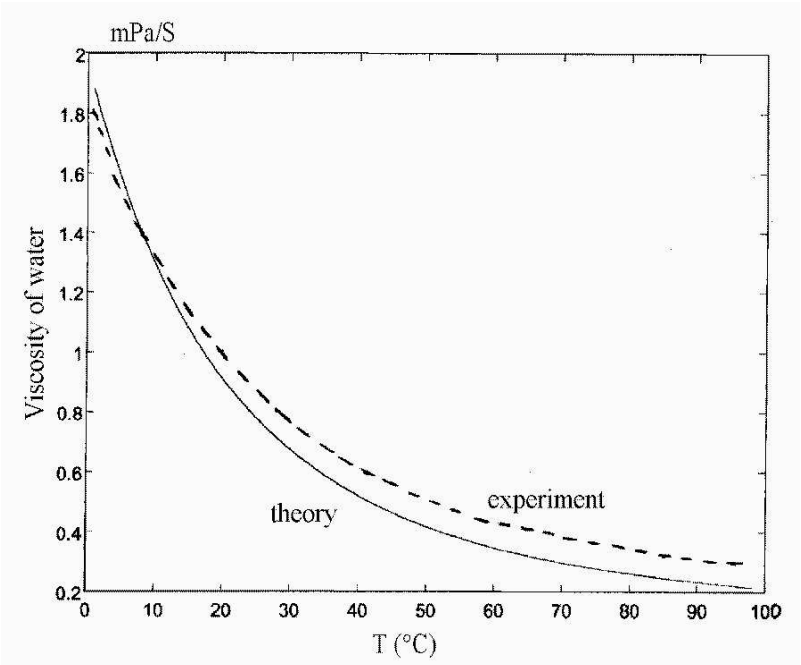

Fig. 18. Theoretical and experimental temperature dependences of viscosities for water. Computer calculations were performed using eqs. (6.44 - 6.53) and (4.3; 4.36).

The best correlation between theoretical and experimental data was achieved after assuming that only $(\pi/2 = 2\pi/4)$ part of the period of above described fluctuation cycles is important for dissipation and viscosity. Introducing this

factor to equations for viscosity calculations gives up very good correspondence between theory and experiment in all temperature interval (0-100^{0}C) for water (Fig.18).

As will be shown below the same factor, introducing the effective time of fluctuations [$\frac{\tau}{\pi/2}$], leads to best results for self-diffusion coefficient calculation.

In the classical hydrodynamic theory the sound absorption coefficient (α) obtained by Stokes includes share (η) and bulk (η_b) averaged microviscosity:

$$\alpha = \frac{\Omega}{2\rho v_s^3}\left(\frac{4}{3}\eta + \eta_b\right), \tag{6.54}$$

where Ω is the angular frequency of sound waves; ρ is the density of liquid.

Bulk viscosity (η_b) is usually calculated from the experimental η and α. It is known that for water:

$$(\eta_b/\eta) \sim 3.$$

The viscosity of solids

In accordance with our model, the biggest fluctuations: *supereffectons and superdeformons* (see Introduction) are responsible for viscosity and diffusion phenomena in solid state. Superdeformons are accompanied by the emergency of cavitational fluctuations in liquids and the defects in solids. The presentation of viscosity formula in solids (η_s) is similar to that for liquids:

$$\eta_S = \frac{E_S}{(\Delta v_f^0)_S}\,\tau_S\left[\frac{T_k}{U_{\rm tot}}\right]^3 \tag{6.55}$$

where: reduced fluctuating volume, related to superdeformons excitation $(\Delta v_f^0)_s$ is:

$$(\Delta v_f^0)_S = \frac{V_0}{N_0 n^2}\frac{1}{Z}P_S \tag{6.56}$$

where: $P_s = (P_D^M)_{tr}\,(P_D^M)_{lb}$ is the relative probability of superdeformons, equal to product of probabilities of *tr and lb* macrodeformons excitation (see 42); $E_s = -kT\,\ln P_s$ is the energy of superdeformons (see Chapter 4);

Characteristic cycle-period of ($A^* \rightleftharpoons B^*$) transition of supereffectons is related to its life-times in A*, B*and transition D* states (see eq.6.46) as was shown

$$\tau_S = \tau_{A^*} + \tau_{B^*} + \tau_{D^*} \tag{6.56a}$$

The viscosity of ice, calculated from eq.(6.55) is bigger than that of water (eq.6.53) to about 10^5 times. This result is in accordance with available experimental data.

6.7. Brownian diffusion

The important formula obtained by Einstein in his theory of Brownian motion is for translational motion of particle:

$$r^2 = 6Dt = \frac{kT}{\pi\eta a}t \tag{6.57}$$

and that for rotational Brownian motion:

$$\varphi^2 = \frac{kT}{4\pi\eta a^3}t \tag{6.58}$$

where: a - radius of spherical particle, much larger than dimension of molecules of liquid. The coefficient of diffusion [D] for Brownian motion is equal to:

$$D = \frac{kT}{6\pi\eta a} \tag{6.59}$$

If we take the angle $\bar{\varphi}^2 = 1/3$ in (6.59), then the corresponding rotational correlation time comes to the form of the known Stokes- Einstein equation:

$$\tau = \frac{4}{3}\pi a^3 \frac{1}{k}\left(\frac{\eta}{T}\right) \tag{6.60}$$

All these formulas (6.57 - 6.60) include macroscopic share viscosity (η) corresponding to our (6.53). In terms of our model, the Brownian movement is a consequence of macrodeformons and convertons. Putting our formula (6.53) for viscosity of liquid into (6.57 - 6.59), we get the possibility of quantitative analysis of corresponding parameters, using our computer program.

6.8. Self-diffusion in liquids and solids

Molecular theory of self-diffusion, as well as general concept of *transfer phenomena* in condensed matter is extremely important, but still unresolved problem.

Simple semi-empirical approach developed by Frenkel leads to following expression for diffusion coefficient in liquid and solid:

$$D = \frac{a^2}{\tau_0}\exp(-W/kT) \tag{6.61}$$

where [a] is the distance of fluctuation jump; $\tau_0 \sim (10^{-12} \div 10^{-13})\, s$ is the average period of molecule oscillations between jumps; W - activation energy of jump.

The parameters: a, τ_0 and W should be considered as a fit parameters.

In accordance with **mesoscopic theory**, the process **of self-diffusion** in liquids**,** like that of **viscosity**, described above, is determined by two contributions:

a) the **collective, nonlocal contribution**, related to translational and librational macrodeformons ($D_{tr,lb}$);

b) the **local contribution,** related to coherent clusters flickering: [dissociation/association] of primary librational effectons (a and b)- convertons ($D_{ac,bc}$).

Each component of the resulting coefficient of self-diffusion (D) in liquid could be presented as the ratio of fluctuation volume cross-section surface: $[\Delta v_f^0]^{2/3}$ to the period of macrofluctuation (τ). The first contribution to coefficient **D,** produced by translational and librational macrodeformons is:

$$D_{tr,lb} = \left[\left(\Delta v_f^0\right)^{2/3} \frac{1}{\tau^M} \right]_{tr,lb} \tag{6.62}$$

where: the surface cross-sections of reduced fluctuating free volumes (see eq.43) fluctuations in composition of macrodeformons (*tr and lb)* are:

$$(\Delta v_f^0)_{tr,lb}^{2/3} = \left[\frac{V_0}{N_0 n^2} \frac{1}{Z} \exp\left(-\frac{\epsilon_D^M}{kT} \right)_{tr,lb} \right]^{2/3} \tag{6.63}$$

$(\tau^M)_{tr,lb}$ are the characteristic ($A \Leftrightarrow B$) cycle-periods of translational and librational macroeffectons (see eqs. 6.46 and 6.47).

The averaged component of self-diffusion coefficient, which takes into account both types of nonlocal fluctuations, related to translational and librational macroeffectons and macrodeformons, can be find as:

$$D^M = [(D)_{tr}^M \, (D)_{lb}^M]^{1/2} \tag{6.64}$$

The formulae for the second, local contribution to self-diffusion in liquids, related to (a and b) convertons ($D_{ac,bc}$) are symmetrical by form to that, presented above for nonlocal processes:

$$D_{ac,bc} = \left[(\Delta v_f^0)^{2/3} \frac{1}{\tau_S} \right]_{ac,bc} \tag{6.65}$$

where: reduced fluctuating free volume of (a and b) convertons $(\Delta v_f^0)_{ac,bc}$ is the same as was used above in mesoscopic theory of viscosity (eq.6.50):

$$(\Delta v_f^0)_{ac,bc} = \frac{V_0}{N_0 n^2} \frac{1}{Z} P_{ac,bc} \tag{6.66}$$

where: P_{ac} and P_{bc} are the relative probabilities of *tr/lib* interconversions between a and b states of translational and librational primary effectons (see Introduction and section 4)

The averaged local component of self-diffusion coefficient, which takes into account both types of convertons (ac and bc) is:

$$D_C = [(D)_{ac} \, (D)_{bc}]^{1/2} \tag{6.67}$$

In similar way we should take into account the contribution of macroconvertons (D_{Mc}):

$$D_{Mc} = \left(\frac{V_0}{N_0 n^2}\frac{1}{Z}P_{Mc}\right)^{2/3}\frac{1}{\tau_{Mc}} \tag{6.67a}$$

where: $P_{Mc} = P_{ac} \cdot P_{bc}$ is a probability of macroconvertons excitation;
the life-time of macroconvertons is:

$$\tau_{Mc} = (\tau_{ac}\,\tau_{bc})^{1/2} \tag{6.67b}$$

The cycle-period of (ac) and (bc) convertons are determined by the sum of life-times of intermediate states of primary translational and librational effectons:

$$\tau_{ac} = (\tau_a)_{tr} + (\tau_a)_{lb}; \quad \text{and} \quad \tau_{bc} = (\tau_b)_{tr} + (\tau_b)_{lb} \tag{6.67c}$$

The life-times of primary and secondary effectons (lb and tr) in a- and b-states are the reciprocal values of corresponding state frequencies:

$$[\tau_a = 1/\nu_a;\ \ \tau_{\overline{a}} = 1/\nu_{\overline{a}};\ \ \text{and} \quad \tau_b = 1/\nu_b;\ \ \tau_{\overline{b}} = 1/\nu_{\overline{b}}]_{tr,lb} \tag{6.67d}$$

$[\nu_a \text{ and } \nu_b]_{tr,lb}$ correspond to eqs. 4.8 and 4.9; $[\nu_{\overline{a}} \text{ and } \nu_{\overline{b}}]_{tr,lb}$ could be calculated using eqs.2.54 and 2.55.

The resulting coefficient of self-diffusion in liquids (D) is a sum of nonlocal (D^M) and local ($D_c,\ D_{Mc}$) effects contributions (see eqs.6.64 and 6.67):

$$D = D^M + D_c + D_{Mc} \tag{6.68}$$

The effective fluctuation-times were taken the same as in previous section for viscosity calculation, using the correction factor $[(\pi/2)\,\tau]$.

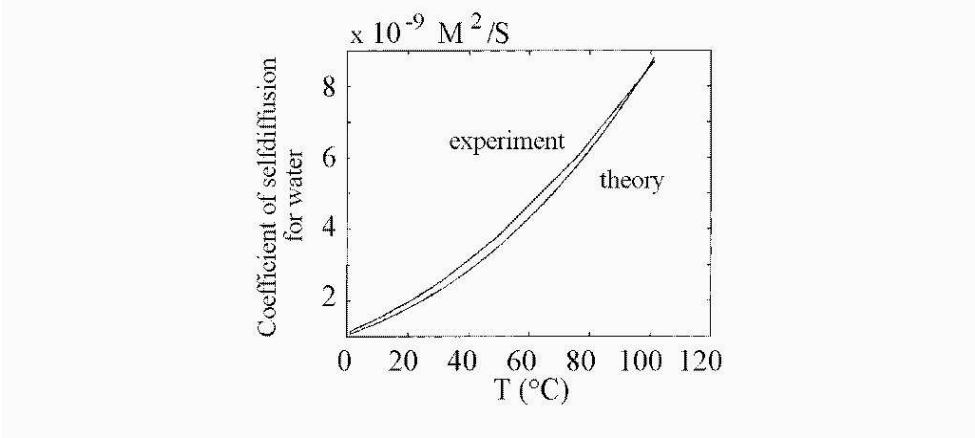

Fig. 19. Theoretical and experimental temperature dependences of self-diffusion coefficients in water. Theoretical coefficient was calculated using eq. 6.68.

Like in the cases of thermal conductivity, viscosity and vapor pressure, the results of theoretical calculations of self-diffusion coefficient coincide well with experimental data for water (Fig. 19) in temperature interval $(0 - 100^0 C)$.

The self-diffusion in solids

In solid state only the biggest fluctuations: *superdeformons,* representing simultaneous excitation of translational and librational macrodeformons in the same volumes of matter are responsible for diffusion and the viscosity phenomena. They are related to origination and migration of the defects in solids. The formal presentation of superdeformons contribution to self-diffusion in solids (D_s) is similar to that of macrodeformons for liquids:

$$D_S = (\Delta v_f^0)_S^{2/3} \frac{1}{\tau_S} \tag{6.69}$$

where: reduced fluctuating free volume in composition of superdeformons $(\Delta v_f^0)_S$ is the same as was used above in mesoscopic theory of viscosity (eq.6.56):

$$(\Delta v_f^0)_S = \frac{V_0}{N_0 n^2} \frac{1}{Z} P_S \tag{6.70}$$

where: $P_S = (P_D^M)_{tr} (P_D^M)_{lb}$ is the relative probability of superdeformons, equal to product of probabilities of *tr and lb* macrodeformons excitation (see 6.42).

Characteristic cycle-period of supereffectons is related to that of *tr and lb* macroeffectons like it was presented in eq.(6.56a):

$$\tau_s = \tau_{A^*} + \tau_{B^*} + \tau_{D^*} \tag{6.71}$$

The self-diffusion coefficient for ice, calculated from eq.6.69 is less than that of water (eq.6.53) to about 10^5 times. This result is in accordance with available experimental data.

Strong decreasing of D in a course of phase transition: [water → ice] predicted by our mesoscopic theory also is in accordance with experiment (Fig. 20).

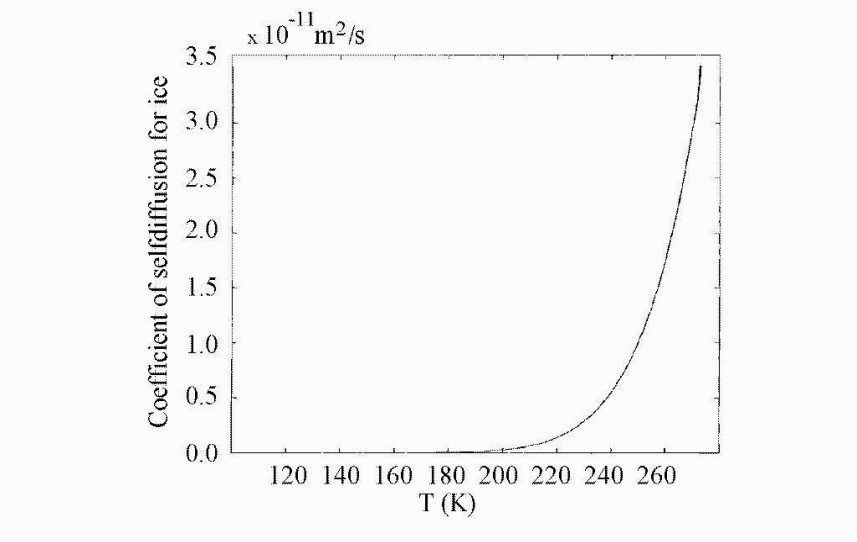

Fig. 20. Theoretical temperature dependences of self-diffusion coefficients in ice.

All these results allow to consider our hierarchic theory of transfer phenomena as a quantitatively confirmed one. They point that the "mesoscopic bridge" between Micro- and Macro Worlds is wide and reliable indeed. It gives a new possibilities for understanding and detailed description of very different phenomena in solids and liquids.

One of the advantages of our theory of viscosity and diffusion is the possibility of explaining numerous nonmonotonic temperature changes, registered by a number of physicochemical methods in various aqueous systems during the study of temperature dependences (Drost-Hansen, 1976; 1992; Johri and Roberts, 1990; Aksnes, Asaad, 1989; Aksnes, Libnau, 1991; Kaivarainen, 1985; Kaivarainen et al., 1993).

Lot of them are related to diffusion or viscosity processes and may be explained by nonmonotonic changes of the refraction index, included in our equations: (6.44, 6.45, 6.50) for viscosity and eqs. (6.69, 6.70) for self-diffusion. For water these temperature anomalies of refraction index were revealed experimentally, using few wave lengths in the temperature interval $3 - 95^0$ (Frontasev, Schreiber, 1966). They are close to Drost-Hansen temperatures. The explanation of these effects, related to periodic variation of primary librational effectons stability with monotonic temperature change was presented as a comments to Fig.4a.

Another consequence of our theory is the elucidation of a big difference between librational η_{lb} (6.48), translational η_{tr} (6.45) viscosities and mesoviscosity, determined by $[lb/tr]$ convertons (6.49 and 6.52).

The effect of mesoviscosity can be checked as long as the volume of a Brownian particle does not exceed much the volume of primary librational effectons

(eq. 6.15). If we take a Brownian particle, much bigger than the librational primary effecton, then its motion will reflect only averaged share viscosity (eq.6.53).

The third consequence of the mesoscopic theory of viscosity is the prediction of nonmonotonic temperature behavior of the sound absorption coefficient α (6.51). Its temperature dependence must have anomalies in the same regions, where the refraction index has.

The experimentally revealed temperature anomalies of (n) also follow from our theory as a result of nonmonotonic $(a \Leftrightarrow b)_{lb}$ equilibrium behavior, stability of primary lb effectons and probability of [lb/tr] convertons excitation (see Discussion to Fig.4a).

Our model predicts also that in the course of transition from the laminar type of flow to the turbulent one the share viscosity (η) will increases due to increasing of structural factor ($T_k/U_{\rm tot}$) in eq. 6.45.

The superfluidity ($\eta \to 0$) in the liquid helium could be a result of inability of this liquid at the very low temperature for translational and librational macroeffectons excitations, i.e. $\tau^M \to 0$.

In turn, it is a consequence of tending to zero the life-times of secondary effectons and deformons in eq.(6.45), responsible for dissipation processes, due to their Bose-condensation and transformation to primary ones (Kaivarainen 1998). The polyeffectons, stabilized by Josephson's junctions between primary effectons form the superfluid component of liquid helium.

7. Osmose and solvent activity. Traditional and mesoscopic approach

It was shown by Van't Hoff in 1887 that osmotic pressure (Π) in the dilute concentration of solute (c) follows a simple expression:

$$\Pi = \ {\rm RTc} \tag{7.1}$$

This formula can be obtained from an *equilibrium condition* between a solvent and an ideal solution after saturation of diffusion process of the solvent through a semipermeable membrane:

$$\mu_1^0(P) = \mu_1(P + \Pi, X_i)$$

where μ_1^0 and μ_1 are the chemical potentials of a pure solvent and a solvent in solution; P - external pressure; Π - osmotic pressure; X_1 is the solvent fraction in solution.

At equilibrium $d\mu_1^0 = d\mu_1 = 0$ and

$$d\mu_1 = \left[\frac{\partial \mu_1}{\partial P_1}\right]_{X_1} dP_1 + \left[\frac{\partial \mu_1}{\partial X_1}\right]_{P_1} dX_1 = 0 \tag{7.1a}$$

Because

$$\mu_1 = \left(\ \partial G/\partial n_1\ \right)_{P,T} = \mu_1^0 + RT \ln X_1 \tag{7.2}$$

then

$$\left(\frac{\partial \mu_1}{\partial P_1}\right)_{X_1} = \left(\frac{\partial^2 G}{\partial P \partial n_1}\right)_{P,T,X} = \left(\frac{\partial V}{\partial n_1}\right) = \overline{V}_1 \tag{7.3}$$

where $\overline{V}_1$ is the partial molar volume of the solvent. For dilute solution: $\bar{V}_1 \simeq V_1^0$ (molar volume of pure solvent).

From (7.2) we have:

$$\frac{\partial \mu_1}{\partial X_1} = RT \left(\frac{\partial \ln X_1}{\partial X_1}\right)_{P,T} \tag{7.4}$$

Putting (7.3) and (7.4) into (7.1a) we obtain:

$$dP_1 = -\frac{RT}{V_1^0 X_1} dX_1$$

Integration:

$$\int_P^{p+\pi} dP_1 = -\frac{RT}{V_1^0} \int_1^{x_1} d \ln X_1 \tag{7.5}$$

gives:

$$\Pi = -\frac{RT}{V_1^0} \ln X_1 = -\frac{RT}{V_1^0} \ln(1 - X_2) \tag{7.6}$$

and for the dilute solution ($X_2 \ll 1$) we finally obtain Van't Hoff equation:

$$\Pi = \frac{RT}{V_1^0} X_2 \cong RT \frac{n_2/n_1}{V_1^0} = \text{ RTc} \tag{7.7}$$

where

$$X_2 = n_2/(n_1 + n_2) \cong n_2/n_1 \tag{7.8}$$

and

$$\frac{n_2/n_1}{V_1^0} = c \tag{7.9}$$

Considering a real solution, we only substitute solvent fraction X_1 in (7.6) by solvent activity: $X_1 \rightarrow a_1$. Then taking into account (7.2), we can express osmotic pressure as follows:

$$\Pi = -\frac{RT}{\bar{V}_1} \ln a_1 = \frac{\Delta\mu_1}{\bar{V}_1} \tag{7.10}$$

where: $\Delta\mu_1 = \mu_1^0$ - μ_1 is the difference between the chemical potentials of a pure solvent and the one perturbed by solute at the starting moment of osmotic process, i.e. the driving force of osmose; $\bar{V}_1 \cong V_1$ is the molar volume of solvent at dilute solutions.

Although the osmotic effects are widespread in Nature and are very important, especially in biology, the physical mechanism of osmose remains unclear (Watterson, 1992).

The explanation following from Van't Hoff equation (7.7) and pointing that osmotic pressure is equal to that induced by solute molecules, if they are considered as an ideal gas in the same volume at a given temperature is not satisfactory.

The osmoses phenomenon can be explained quantitatively on the basis of our mesoscopic theory and state equation (see 6.6 and 6.7). To this end, we have to introduce the rules of conservation of the main internal parameters of solvent in the presence of guest (solute) molecules or particles:

$$\left.\begin{array}{l} 1.\ \text{Internal pressure of solvent: } P_{\text{in}} = \text{ const} \\ 2.\ \text{The total energy of solvent: } U_{\text{tot}} = \text{ const} \end{array}\right\} \tag{7.11}$$

This conservation rules can be considered as the consequence of Le Chatelier principle.

Using (6.6), we have for the pure solvent and the solvent perturbed by a solute the following two equations, respectively:

$$P_{\text{in}} = \frac{U_{\text{tot}}}{V_{fr}^0}\left(1 + \frac{V}{T_k}\right) - P_{\text{ext}} \tag{7.12}$$

$$P_{\text{in}}^1 = \frac{U_{\text{tot}}^1}{V_{fr}^1}\left(1 + \frac{V_1}{T_k^1}\right) - P_{\text{ext}}^1, \tag{7.13}$$

where:

$$V_{fr}^0 = \frac{V_0}{n^2} \quad \text{and} \quad V_{fr}^1 = \frac{V_0}{n_1^2} \tag{7.14}$$

are the free volumes of pure solvent and solvent in presence of solute (guest) molecules as a ratio of molar volume of solvent to correspondent value of refraction index.

The equilibrium conditions *after osmotic process saturation*, leading from our conservation rules (7.11) are

$$P_{\text{in}} = P_{\text{in}} \quad \text{when} \quad P_{\text{ext}} = P_{\text{ext}} + \Pi \tag{7.15}$$

$$U_{\text{tot}} = V + T_k = V_1 + T_k^1 = U_{\text{tot}}^1 \tag{7.16}$$

From (7.16) we have:

$$\text{Dif } = T_k - T_k^1 = V_1 - V \tag{7.17}$$

The index $^{(1)}$ denote perturbed solvent parameters.

Comparing (7.12) and (7.13) and taking into account (7.14 - 7.16), we obtain a new formula for osmotic pressure:

$$\Pi = \frac{n^2}{V_0} U_{\text{tot}} \left[\frac{n_1^2 T_k - n^2 T_k^1}{T_k T_k^1} \right] \tag{7.18}$$

where: n, V_0, U_{tot} and T_k are the refraction index, molar volume, total energy and total kinetic energy of a pure solvent, respectively; T_k^* and n_1 are the total kinetic energy and refraction index of the solvent in the presence of guest (solute) molecules; T_k and T_k^* can be calculated from our theory (eq.4.36).

For the case of dilute solutions, when $T_k T_k^1 \cong T_k^2$ and $n \cong n_1$, the eq.(7.18) can be simplified:

$$\Pi = \frac{n^2}{V_0} \left(\frac{U_{\text{tot}}}{T_k} \right)^2 \left(T_k - T_k^1 \right) \tag{7.19}$$

or using (7.17):

$$\Pi = \frac{n^2}{V_0} \left(\frac{U_{\text{tot}}}{T_k} \right)^2 (V_1 - V) \tag{7.20}$$

The ratio:

$$S = T_k / U_{\text{tot}} \tag{7.21}$$

is generally known as a structural factor.

We can see from (7.19) and (7.20) that osmotic pressure is proportional to the difference between total kinetic energy of a free solvent (T_k) and that of the solvent perturbed by guest molecules:

$$\Delta T_k = T_k - T_k^1$$

or related difference between the total potential energy of perturbed and pure solvent:

$\Delta V = V_1 - V$ where: $\Delta T_k = \Delta V \equiv \text{Dif}$ (see Fig. 21).

As far $\Delta \text{T}_k > 0$ and $\Delta V > 0$, it means that:

$$\begin{gathered} T_k > T_k^1 \\ \text{or} \\ V_1 > V \end{gathered} \tag{7.22}$$

Theoretical temperature dependence of the difference

$$Dif = \Delta T_k = \Delta V$$

calculated from (7.19) or (7.20) at constant osmotic pressure: $\Pi \equiv Pos = 8$ atm., pertinent to blood is presented on Fig. 21.

The next Fig. 22 illustrate theoretical temperature dependence of osmotic pressure (7.20) in blood at the constant value of $\mathbf{Dif} = 6.7 \cdot 10^{-3}(J/M)$, corresponding on Fig. 21 to physiological temperature (37^0).

The ratios of this **Dif** value to total potential (V) and total kinetic energy (T_k) of pure water at 37^0(see Fig. 21) are equal to:

$$(\mathrm{Dif}/V) \simeq \frac{6.7 \cdot 10^{-3}}{1.3 \cdot 10^4} \cong 5 \cdot 10^{-7} \quad \text{and}$$
$$(\mathrm{Dif}/T_k) \simeq \frac{6.7 \cdot 10^{-3}}{3.5 \cdot 10^2} \cong 2 \cdot 10^{-5}$$

i.e. the relative changes of the solvent potential and kinetic energies are very small.

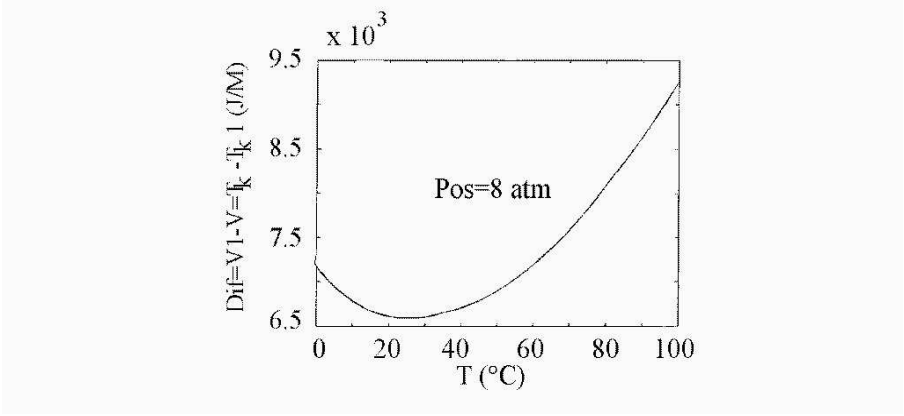

Fig. 21. Theoretical temperature dependence of the difference: $\mathbf{Dif} = V_1 - V = T_k - T_k^1$ at constant osmotic pressure: $\Pi \equiv Pos = 8$ atm., characteristic for blood. The computer calculations were performed using eqs. (7.19) or (7.20).

For each type of *concentrated macromolecular solutions the optimum amount of water is needed to minimize the potential energy of the system* determined mainly by clusterphilic interactions. The conservation rules (7.11) and self-organization in solutions of macromolecules (clustron formation) may be responsible for the *driving force of osmose* in the different compartments of biological cells.

Comparing (7.20) and (7.10) and assuming equality of the molar volumes $V_0 = \bar{V}_1$, we find a relation between the difference in potential energies and chemical potentials ($\Delta\mu$) of unperturbed solvent and that perturbed by the solute:

$$\Delta\mu = \mu_1^0 - \mu_1 = n^2 \left(\frac{U_{\rm tot}}{T_k}\right)^2 (V_1 - V) \tag{7.23}$$

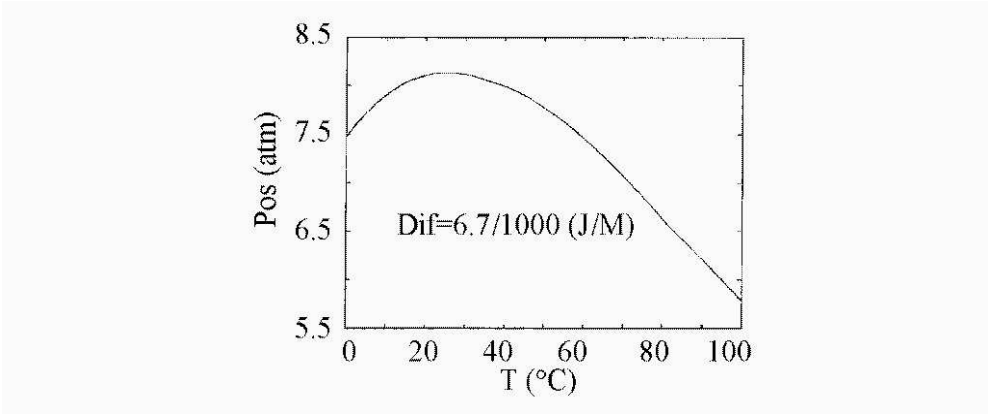

Fig. 22. Theoretical temperature dependence of osmotic pressure (eq. 43) in blood at constant value of difference: Dif = $\Delta T = \Delta V = 6.7 \cdot 10^{-3} J/\mathrm{M}$. This value in accordance with Fig.3 corresponds to physiological temperature (37^0).

The results obtained above mean that solvent activity (a_1) **and a lot of other thermodynamic parameters for solutions can be calculated on the basis of our hierarchic concept:**

$$a_1 = \exp\left(-\frac{\Delta\mu}{RT}\right) = \exp\left[-\left(\frac{n}{S}\right)^2 \frac{V_1 - V}{RT}\right] \tag{7.24}$$

where: $S = T_k/U_{\rm tot}$ is a structural factor for the solvent.
The molar coefficient of activity is:

$$y_i = a_i/c_i, \tag{7.25}$$

where

$$c_i = n_i/V \tag{7.26}$$

is the molar quantity of i-component (n_i) in of solution (V - solution volume in liters).

The molar activity of the solvent in solution is related to its vapor pressure (P_i) as:

$$a_i = P_i/P_i^0 \tag{7.27}$$

where: P_i^0 is the vapor pressure of the pure solvent. Theoretical temperature dependence of water activity (a_1) in blood at constant difference: Dif = $\Delta T = \Delta V = 6.7 \cdot 10^{-3} J/M$ is presented on Fig. 23.

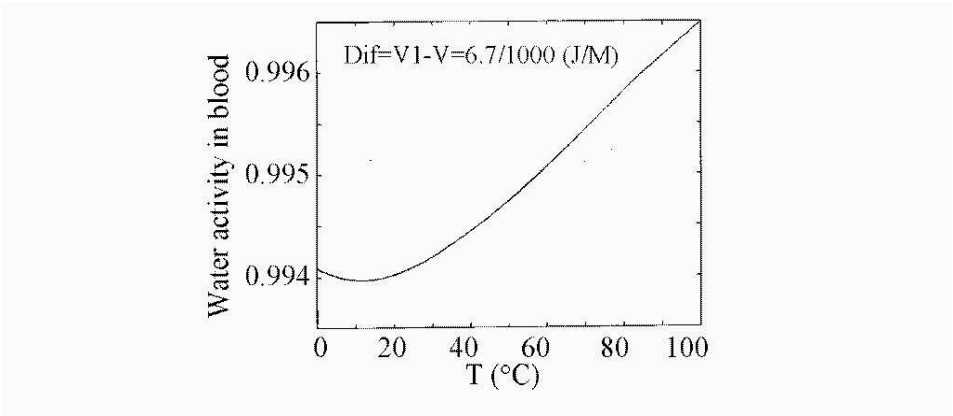

Fig. 23. Theoretical temperature dependence of water activity (a_1) (*eq.*7.24) in blood at constant difference: $Dif = \Delta T = \Delta V = 6.7 \cdot 10^{-3} J/M$.

Another *colligative parameter* such as low temperature shift of freezing temperature of the solvent (ΔT_f) in the presence of guest molecules also can be calculated from (7.24) and the known relation (7.28a) between water activity in solution and (ΔT_f):

$$\Delta T_f = -\frac{R(T_f^0)^2}{\Delta H} \ln a_1 \frac{(T_f^0)^2}{\Delta H\, T} \left(\frac{n}{S}\right)^2 (V_1 - V) \tag{7.28}$$

where:T_f^0 is the freezing temperature of the pure solvent; T is the temperature at conditions of calculations of potential energies $V_1(T)$ and $V(T)$ from eqs. 4.36 and 4.39;

$$\ln a_1 = -[\triangle H / R(T_f^0)^2] \triangle T_f \tag{7.28a}$$

The partial molar enthalpy ($\bar{H}_1$) of solvent in solution are related to solvent activity like:

$$\overline{H}_1 = \overline{H}_1^0 - RT^2 \frac{\partial \ln a_1}{\partial T} = \overline{H}_1^0 + \overline{L}_1^0 \tag{7.29}$$

where $\overline{H}_1^0$ is the partial enthalpy of the solvent at infinitive dilution;

$$\bar{L}_1 = -RT^2 \frac{\partial \ln a_1}{\partial T} = T^2 \frac{\partial}{\partial T} \left[\left(\frac{n}{S}\right)^2 \frac{V_1 - V}{T} \right] \tag{7.30}$$

is the relative partial **molar enthalpy of solvent** in a given solution.
From (7.29) we obtain partial molar heat capacity as:

$$C_p^1 = \frac{\partial}{\partial T}(H_1) = C_p^0 - R \left(T^2 \frac{\partial^2 \ln a_1}{\partial T^2} + 2T \frac{\partial \ln a_1}{\partial T} \right) \tag{7.31}$$

An analogous equation exists for the *solute* of this solution as well as for partial *molar volume* and other important parameters of the solvent, *including solvent activity* (Godnev et al., 1982).

It is obvious, the application of Hierarchic theory to solvent activity evaluation might be of practical importance for different processes in chemical and colloid technology.

8. New approach to theory of light refraction

8.1. Refraction in gas

If the action of photons onto electrons of molecules is considered as a force, activating a harmonic oscillator with decay, it leads to the known classical equations for a complex refraction index (Vuks, 1984).

The Lorentz-Lorenz formula obtained in such a way is convenient for practical needs. However, it does not describe the dependence of refraction index on the incident light frequency and did not take into account the intermolecular interactions. In the new theory proposed below we have tried to clear up the relationship between these parameters.

Our basic idea is that the dielectric penetrability of matter ϵ, (equal in the optical interval of frequencies to the refraction index squared n^2), is determined by the ratio of partial volume energies of photon in vacuum to similar volume energy of photon in matter:

$$\epsilon = n^2 = \frac{[E_p^0]}{[E_p^m]} = \frac{m_p c^2}{m_p c_m^2} = \frac{c^2}{c_m^2} \tag{8.1}$$

where $m_p = h\nu_p/c^2$ is the effective photon mass, c is the light velocity in vacuum, c_m is the effective light velocity in matter.

We introduce the notion of partial volume energy of a photon in vacuum $[E_p^0]$ and in matter $[E_p^m]$ as a product of photon energy ($E_p = h\nu_p$) and the volume (V_p) occupied by 3D standing wave of photon in vacuum and in matter, correspondingly:

$$[E_p^0] = E_p V_p^0 \qquad [E_p^m] = E_p V_p^m \tag{8.2}$$

The 3D standing photon volume as an interception volume of 3 different standing photons normal to each other was termed in our mesoscopic model as a primary electromagnetic deformon (see Introduction).

In vacuum, where the effect of an excluded volume due to the spatial incompatibility of electron shells of molecules and photon is absent, the volume of $3D$ photon standing wave (primary deformon) is:

$$V_p^0 = \frac{1}{n_p} = \frac{3\lambda_p^2}{8\pi} \tag{8.3}$$

We will consider the interaction of light with matter in this mesoscopic volume, containing a thousands of molecules of condensed matter. It is the reason why we titled this theory of light refraction as mesoscopic one.

Putting (8.3) into (8.2), we obtain the formula for the partial volume energy of a photon in vacuum:

$$[E_p^0] = E_p V_p^0 = h\nu_p \frac{9\lambda_p^2}{8\pi} = \frac{9}{4}\hbar c \lambda_p^2 \tag{8.4}$$

Then we proceed from the assumption that waves B of photons can not exist with waves B of electrons, forming the shells of atoms and molecules in the same space elements. Hence, the effect of excluded volume appears during the propagation of an external electromagnetic wave through the matter. It leads to the fact that in matter the volume occupied by a photon, is equal to

$$V_p^m = V_p^0 - V_p^{\text{ex}} = V_p^0 - n_M^p \cdot V_e^M \tag{8.5}$$

where $V_p^{\text{ex}} = n_M^p V_e^M$ is the excluded volume which is equal to the product of the number of molecules in the volume of one photon standing wave (n_M^p) and the volume occupied by the electron shell of one molecule (V_e^M).

n_M^p is determined by the product of the volume of the photons 3D standing wave in the vacuum (8.3) and the concentration of molecules ($n_M = N_0/V_0$):

$$n_M^p = \frac{9\lambda_p^3}{8\pi}\left(\frac{N_0}{V_0}\right) \tag{8.6}$$

In the absence of the polarization by the external field and intermolecular interaction, the volume occupied by electrons of the molecule:

$$V_e^M = \frac{4}{3}\pi L_e^3 \tag{8.7}$$

where L_e is the radius of the most probable wave B ($L_e = \lambda_e/2\pi$) of the outer electron of a molecule. As it has been shown in (7.5) that the mean molecule polarizability is:

$$\alpha = L_e^3 \tag{8.8}$$

Then taking (8.7) and (8.6) into account, the excluded volume of primary electromagnetic deformon in the matter is:

$$V_p^{\text{ex}} = \frac{9\lambda_p^3}{8\pi} n_M \frac{4}{3}\pi\alpha = \frac{3}{2}\lambda_p^3 n_M \alpha \tag{8.9}$$

Therefore, the partial volume energy of a photon in the vacuum is determined by eq.(8.4), while that in matter, according to (8.5):

$$[E_p^m] = E_p\, V_p^m = E_p\, [V_p^0 - V_p^{\text{ex}}] \tag{8.10}$$

Putting (8.4) and (8.10) into (8.1) we obtain:

$$\epsilon = n^2 = \frac{E_p V_p^0}{E_p(V_p^0 - V_p^{\rm ex})} \tag{8.11}$$

or

$$\frac{1}{n^2} = 1 - \frac{V_p^{\rm ex}}{V^0} \tag{8.12}$$

Then, putting eq.(8.9) and (8.3) into (8.12) we derive new equation for refraction index, leading from our mesoscopic theory:

$$\frac{1}{n^2} = 1 - \frac{4}{3}\pi n_M \alpha \tag{8.13}$$

or in another form:

$$\frac{n^2-1}{n^2} = \frac{4}{3}\pi n_M \alpha = \frac{4}{3}\pi \frac{N_0}{V_0}\alpha \tag{8.14}$$

where: $n_M = N_0/V_0$ is a concentration of molecules;

In this equation $\alpha = L_e^3$ is the average static polarizability of molecules for the case when the external electromagnetic fields as well as intermolecular interactions inducing the additional polarization are absent. This situation is realized at $E_p = h\nu_p \to 0$ and $\lambda_p \to \infty$ in the gas phase. As will be shown below the value of resulting α^* in condensed matter is bigger.

8.2. Light refraction in liquids and solids

According to the Lorentz classical theory, the electric component of the outer electromagnetic field is amplified by the additional inner field ($E_{\rm ad}$), related to the interaction of induced dipole moments in composition of condensed matter with each other:

$$E_{\rm ad} = \frac{n^2-1}{3}E \tag{8.15}$$

The mean Lorentz *acting field* $\bar{F}$ can be expressed as:

$$\overline{F} = E + E_{\rm ad} = \frac{n^2+2}{3}E \quad (\text{at } \ n \to 1, \ \overline{F} \to E) \tag{8.16}$$

$\bar{F}$- has a dimensions of electric field tension and tends to E in the gas phase when $n \to 1$.

In accordance with our model, beside the Lorentz acting field, the total internal acting field, includes also two another contributions, increasing the molecules polarizability (α) in condensed matter:

1. Potential intermolecular field, including all the types of Van- der-Waals interactions in composition of coherent collective excitations, even without external electromagnetic field. Like total potential energy of matter, this contribution must be dependent on temperature and pressure;

2. Primary internal field, related with primary electromagnetic deformons (tr and lb). This component of the total acting field also exist without external fields. Its frequencies corresponds to IR range and its action is much weaker than the action of the external visible light.

Let us try to estimate the energy of the total acting field and its effective frequency (ν_f) and wavelength (λ_f), that we introduce as:

$$A_f = h\nu_f = \frac{hc}{\lambda_f} = A_L + A_V + A_D \tag{8.17}$$

where: A_L, A_V and A_D are contributions, related with Lorentz field, potential field and primary deformons field correspondingly.

When the interaction energy of the molecule with a photon ($E_p = h\nu_p$) is less than the energy of the resonance absorption, then it leads to elastic polarization of the electron shell and origination of secondary photons, i.e. light scattering. We assume in our consideration that the increment of polarization of a molecule (α) under the action of the external photon ($h\nu_p$) and the total active field ($A_f = h\nu_f$) can be expressed through the increase of the most probable radius of the electron's shell ($L_e = \alpha^{1/3}$), using our (eq. 7.6 from [Kaivarainen, 1995, 2000]):

$$\Delta L_e = \frac{\omega_p\, m_e}{2\hbar}\alpha \tag{8.18}$$

where the resulting increment:

$$\Delta L^* = \Delta L_e + \Delta L_f = \frac{(h\nu_p + A_f)m_e}{2\hbar^2}\alpha \tag{8.18a}$$

where: $\alpha = L_e^3$ is the average polarizability of molecule in gas phase at $\nu_f \rightarrow 0$.

For water molecule in the gas phase:

$$L_e = \alpha^{1/3} = 1.13 \cdot 10^{-10}\, m$$

is a known constant, determined experimentally [4].

The total increment of polarizability radius (ΔL^*) and resulting polarizability of molecules (α^*) in composition of condensed matter affected by the acting field

$$\alpha^* = (L^*)^3 \tag{8.18b}$$

can be find from the experimental refraction index (n) using our formula (8.14):

$$L^* = (\alpha^*)^{1/3} = \left[\frac{3}{4\pi}\frac{V_0}{N_0}\frac{n^2-1}{n^2}\right]^{1/3} \tag{8.19}$$

$$\Delta L^* = L^* - L_e \tag{8.20}$$

from (8.18) we get a formula for the increment of radius of polarizability (ΔL_f), induced by the total internal acting field:

$$\Delta L_f = \Delta L^* - \Delta L_e = \frac{A_f\, m_e}{2\hbar^2}\alpha \tag{8.21}$$

Like total internal acting field energy (8.17), this total acting increment can be presented as a sum of contributions, related to Lorentz field (ΔL_F), potential field (ΔL_V) and primary deformons field (ΔL_D):

$$\Delta L_f = \Delta L_L + \Delta L_V + \Delta L_D \tag{8.22}$$

Increment ΔL_e, induced by external photon only, can be calculated from the known frequency (ν_p) of the incident light (see 8.18a):

$$\Delta L_e = \frac{h\nu_p\, m_e}{2\hbar^2}\alpha \tag{8.23}$$

It means that ΔL_f can be found from (8.21) and (8.17), using (8.23). Then from (8.21) we can calculate the energy (A_f), effective frequency (ν_f) and wave length (λ_f) of the total acting field like:

$$A_f = h\nu_f = hc/\lambda_f = 2\frac{\Delta L_f\,\hbar^2}{m_e\alpha} \tag{8.24}$$

The computer calculations of α^*; $L^* = L_e + \Delta L^* = (\alpha^*)^{1/3}$ and A_f in the temperature range $(0 - 95^0)$ are presented on Fig.24.

One must keep in mind that in general case α and L are tensors. It means that all the increments, calculated on the base of eq.(8.18a) must be considered as the effective ones. Nevertheless, it is obvious that our approach to analysis of the acting field parameters can give useful additional information about the properties of transparent condensed matter.

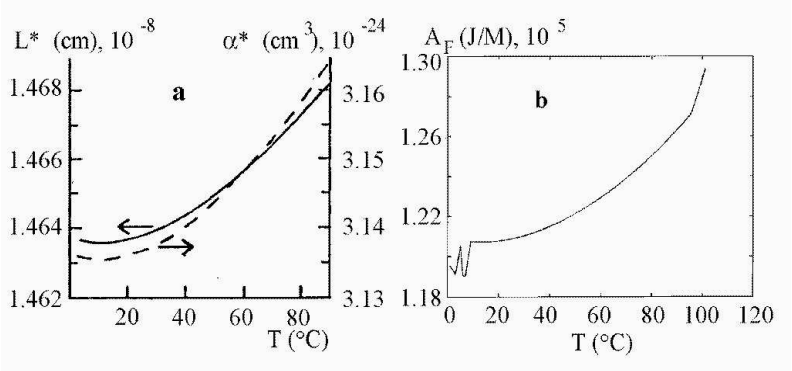

Fig. 24. (a)- Temperature dependencies of the most probable outer electron shell radius of H_2O (L^*) and the effective polarizability $\alpha^* = (L^*)^3$ in the total acting field (eq. 8.19);

(b)- Temperature dependence of the total acting field (A_f) energy (8.24) in water at the wavelength of the incident light $\lambda_p = 5.461 \cdot 10^{-5} cm^{-1}$. The experimental data for refraction index $n(t)$ were used in calculations. The initial electron shell radius is: $L_e = \alpha_{H2O}^{1/3} = 1.13 \cdot 10^{-8} cm$. In graphical calculations in Fig.24a, the used experimental temperature dependence of the water refraction index were obtained by Frontas'ev and Schreiber (1966).

The temperature dependencies of these parameters were computed using the known experimental data on refraction index $n(t)$ for water and presented in Fig.24a. The radius L^* in the range $0 - 95^0 C$ increases less than by 1% at constant incident light wavelength ($\lambda = 546.1 nm$). The change of ΔL_f with temperature is determined by its potential field component change ΔL_V.

The relative change of this component: $\Delta\Delta L_V / \Delta L_f$ ($t = 0^0 C$) is about 9%. Corresponding to this change the increasing of the acting field energy A_f (eq.8.23) increases approximately by $8\, kJ/M$ (Fig 8.1 b) due to its potential field contribution.

It is important that the total potential energy of water in the same temperature range, according to our calculations, increase by the same magnitude (Fig. 3b). This fact points to the strong correlation between potential intermolecular interaction in matter and the value of the acting field energy.

It was calculated that, at constant temperature (20^0) the energy of the acting field (A_f), (eq.8.23) in water practically does not depend on the wavelength of incident light (λ_p). At more than three time alterations of λ_p: from $12.56 \cdot 10^{-5} cm$ to $3.03 \cdot 10^{-5} cm$ when the water refraction index (n) changes from 1.320999 to 1.358100 (Kikoin, 1976), the value of A_f changes less than by 1%.

At the same conditions the electron shell radius L* and the acting polarizability α^* thereby increase from (1.45 to 1.5)$\cdot 10^{-10}$ m and from (3.05 to 3.274) $\cdot 10^{-30} m^3$ respectively (Fig.25). These changes are due to the incident photons action only. For water molecules in the gas phase and $\lambda_p \to \infty$ the initial polarizability ($\alpha = L_e^3$) is equal to $1.44 \cdot 10^{-24} cm^3$ (Eisenberg, Kauzmann,1969), i.e. significantly less than in condensed matter under the action of external and internal fields.

Obviously, the temperature change of energy A_f (Fig.24b) is determined by the internal pressure increasing (section ..), related to intermolecular interaction change, depending on mean distances between molecules and, hence, on the concentration (N_0/V_0) of molecules in condensed matter.

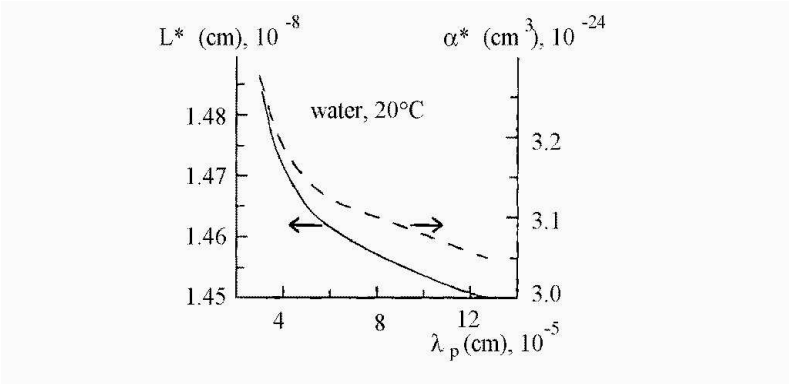

Fig. 25. Dependencies of the acting polarizability $\alpha^* = (L^*)^3$ and electron shell radius of water in the acting field (L^*) on incident light wavelength (λ_p), calculated from eq. (8.14) and experimental data $n(\lambda_p)$ (Kikoin, 1976). The initial polarizability of H_2O in the gas phase at $\lambda_p \to \infty$ is equal to $\alpha = L_e^3 = 1.44 \cdot 10^{-24} cm^3$. The corresponding initial radius of the H_2O electron shell is $L_e = 1.13 \cdot 10^{-8} cm$.

On the basis of our data, changes of A_f, calculated from (8.24) are caused mainly by the heat expansion of the matter. The photon induced increment of the polarizability ($\alpha \to \alpha^*$) practically do not change A_f.

The ability to obtain new valuable information about changes of molecule polarizability under the action of incident light and about temperature dependent molecular interaction in condensed medium markedly reinforce such a widely used method as refractometry.

The above defined relationship between the molecule polarizability and the wave length of the incident light allows to make a new endeavor to solve the light scattering problems.

9. Mesoscopic theory of Brillouin light scattering in condensed matter

9.1. Traditional approach

According to traditional concept, light scattering in liquids and crystals as well as in gases takes place due to random heat fluctuations. In condensed media the fluctuations of density, temperature and molecule orientation are possible.

Density (ρ) fluctuations leading to dielectric penetrability (ϵ) fluctuations are of major importance. This contribution is estimated by means of Einstein formula for scattering coefficient of liquids:

$$R = \frac{Ir^2}{I_0 V} = \frac{\pi}{2\lambda^4} kT\beta_T \left(\rho \frac{\partial \epsilon}{\partial \rho}\right)_T \tag{9.1}$$

where β_T is isothermal compressibility.

Many authors made attempts to find a correct expression for the variable $(\rho\frac{\partial\epsilon}{\partial\rho})$.

The formula derived by Vuks (1977, 1984) is most consistent with experimental data:

$$\rho\frac{\partial\epsilon}{\partial\rho} = (n^2-1)\frac{3n^2}{2n^2-1} \tag{9.2}$$

9.2. Fine structure of scattering

The fine structure - spectrum of the scattering in liquids is represented by two Brillouin components with frequencies shifted relatively from the incident light frequency: $\nu_\pm = \nu_0 \pm \Delta\nu$ and one unshifted band like in gases (ν_0).

The shift of the Brillouin components is caused by the Doppler effect resulting from a fraction of photons scattering on phonons moving at sound speed in two opposite directions.

This shift can be explained in different way as well (Vuks, 1977). If in the antinodes of the standing wave the density oscillation occurs at frequency (Ω):

$$\rho = \rho_0 \cos\Omega t, \tag{9.3}$$

then the scattered wave amplitude will change at the same frequency. Such a wave can be represented as a superposition of two monochromatic waves having the frequencies:$(\omega+\Omega)$ and $(\omega-\Omega)$, where

$$\Omega = 2\pi f \tag{9.4}$$

is the elastic wave frequency at which scattering occurs when the Wolf-Bragg condition is satisfied:

$$2\Lambda\sin\varphi = 2\Lambda\sin\frac{\theta}{2} = \lambda^{'} \tag{9.5}$$

or

$$\Lambda = \lambda'/(2\sin\frac{\theta}{2}) = \frac{c}{n\nu}(2\sin\frac{\theta}{2}) = v_{ph}/f \tag{9.6}$$

where Λ is the elastic wave length corresponding to the frequency f; $\lambda^{'} = \lambda/n = c/n\nu$ (λ' and λ are the incident light wavelength in matter and vacuum, respectively); φ is the angle of sliding; θ is the angle of scattering; n is the refraction index of matter; c is the light speed.

The value of Brillouin splitting is represented as:

$$\pm\Delta\nu_{M-B} = f = \frac{V_{ph}}{\Lambda} = 2\nu\frac{V_{ph}}{c}n\sin\frac{\theta}{2} \tag{9.7}$$

where: $\nu n/c = 1/\lambda$; n is the refraction index of matter; ν is incident light frequency;

$$v_{ph} = v_S \tag{9.8}$$

is the phase velocity of a scattering wave equal to hypersonic velocity.

The formula (9.7) is identical to that obtained from the analysis of the Doppler effect:

$$\frac{\Delta\nu}{\nu} = \pm 2\frac{V_S}{c} n \sin\frac{\theta}{2} \tag{9.9}$$

According to the classical theory, the central line, which is analogous to that observed in gases, is caused by entropy fluctuations in liquids, without any changes of pressure (Vuks, 1977). On the basis of Frenkel theory of liquid state, the central line can be explained by fluctuations of "hole" number - cavitational fluctuations (Theiner, 1969).

The thermodynamic approach of Landau and Plachek leads to the formula, which relates the intensities of the central (I) and two lateral (I_{M-B}) lines of the scattering spectrum with compressibility and heat capacities:

$$\frac{I}{2I_{M-B}} = \frac{I_p}{I_{\text{ad}}} = \frac{\beta_T - \beta_S}{\beta_S} = \frac{C_p - C_v}{C_v} \tag{9.10}$$

where: β_T and β_S are isothermal and adiabatic compressibilities; C_p and C_v are isobaric and isohoric heat capacities.

In crystals, quartz for example, the central line in the fine structure of light scattering is usually absent or very small. However, instead of one pair of shifted components, observed in liquids, there appear *three* Brillouin components in crystals. One of them used to be explained by scattering on the longitudinal phonons, and two - by scattering on the transversal phonons.

9.3. New mesoscopic approach to problem

In follows from our hierarchic theory that the thermal "random" fluctuations are "organized" by different types of superimposed quantum excitations.

According to our Hierarchic model, including microscopic, mesoscopic and macroscopic scales of matter (see Introduction), the most probable (primary) and mean (secondary) effectons, translational and librational are capable of quantum transitions between two discreet states: $(a \Leftrightarrow b)_{tr,lb}$ and $(\bar{a} \Leftrightarrow \bar{b})_{tr,lb}$ respectively. These transitions lead to origination/annihilation of photons and phonons, forming primary and secondary deformons.

The mean heat energy of molecules is determined by the value of 3kT, which as our calculations show, has the intermediate value between the discreet energies of a and b quantum states of primary effectons (Fig...), making, consequently, the non-equilibrium conditions in condensed matter. Such kind of instability is a result of "competition" between classical and quantum distributions of energy .

The maximum deviations from thermal equilibrium and that of the dielectric properties of matter occur when the same states of primary and secondary quasiparticles, e.g. $a,\bar{a}$ and $b,\bar{b}$ occur simultaneously. Such a situation corresponds to the A and B states of macroeffectons. The $(A \Leftrightarrow B)_{tr,lb}$ transitions represent thermal fluctuations. The big density fluctuations are related to "flickering clusters" (macroconvertons between librational and translational primary effectons) and the maximum fluctuations correspond to Superdeformons.

Only in the case of spatially independent fluctuations the interference of secondary scattered photons does not lead to their total compensation.

The probability of the event that two spatially uncorrelated events coincide in time is equal to the product of their independent probabilities.

Thus, the probabilities of the coherent $(a,\bar{a})$ and $(b,\bar{b})$ states of primary and secondary effectons, corresponding to A and B states of the macroeffectons (tr and lb), independent on each other, are equal to:

$$\left(\ P_M^A\ \right)_{tr,lb}^{\mathrm{ind}} = \left(\ P_{ef}^a \bar{P}_{ef}^a\ \right)_{tr,lb}^{S} \left(\frac{1}{Z^2}\right) = \left(\frac{P_M^A}{Z^2}\right)_{tr,lb} \tag{9.11}$$

$$\left(P_M^B\right)_{tr,lb}^{\mathrm{ind}} = \left(\ P_{ef}^b \bar{P}_{ef}^b\ \right)_{tr,lb}^{S} \left(\frac{1}{Z^2}\right) = \left(\frac{P_M^B}{Z^2}\right)_{tr,lb} \tag{9.12}$$

where

$$\frac{1}{Z}\left(P_{ef}^a\right)_{tr,lb} \quad \text{and} \quad \frac{1}{Z}\left(\bar{P}_{ef}^a\right)_{tr,lb} \tag{9.13}$$

are the independent probabilities of a and $\bar{a}$ states determined according to formulae (4.10 and 4.18), while probabilities $\left(P_{ef}^b/Z\right)_{tr,lb}$ and $\left(\bar{P}_{ef}^b/Z\right)_{tr,lb}$ are determined according to formulae (4.11 and 4.19);

Z is the sum of probabilities of all types of quasiparticles states - eq.(4.2).

The probabilities of molecules being involved in the spatially independent translational and librational macrodeformons are expressed as the products (9.11) and (9.12):

$$\left(\ P_D^M\ \right)_{tr,lb}^{\mathrm{ind}} = \left[\ \left(\ P_M^A\ \right)^{\mathrm{ind}} \left(\ P_M^B\ \right)^{\mathrm{ind}}\ \right]_{tr,lb} = \frac{P_D^M}{Z^4} \tag{9.14}$$

Formulae (9.11) and (9.12) may be considered as the probabilities of space-independent but coherent macroeffectons in A and B states, respectively.

For probabilities of space-independent supereffectons in A^* and B^* states we have:

$$\left(\ P_S^{A^*}\ \right)^{\mathrm{ind}} = \left(\ P_M^A\ \right)_{tr}^{\mathrm{ind}} \left(\ P_M^A\ \right)_{lb}^{\mathrm{ind}} = \frac{P_S^{A^*}}{Z^4} \tag{9.15}$$

$$\left(\ P_S^{B^*}\ \right)^{\mathrm{ind}} = \left(\ P_M^B\ \right)_{tr}^{\mathrm{ind}} \left(\ P_M^B\ \right)_{tr}^{\mathrm{ind}} = \frac{P_S^{b^*}}{Z^4} \tag{9.15a}$$

In a similar way we get from (9.14) the probabilities of spatially independent superdeformons:

$$\left(\ P_S^{D^*} \ \right)^{\text{ind}} = \left(\ P_M^D \ \right)_{tr} \left(\ P_M^D \ \right)_{lb} = \frac{P_S^{D^*}}{Z^4} \tag{9.16}$$

The concentrations of molecules, the states of which markedly differ from the equilibrium one and which cause light scattering in composition of spatially independent macroeffectons and macrodeformons, are equal to:

$$\left[N_M^A = \frac{N_0}{Z^2 V_0} \left(\ P_M^A \ \right) \right]_{tr,lb}; \quad \left[N_M^B = \frac{N_0}{Z^2 V_0} \left(\ P_M^B \ \right) \right]_{tr,lb} \tag{9.17}$$

$$\left[N_M^D = \frac{N_0}{Z^4 V_0} \left(\ P_M^D \ \right) \right]_{tr,lb}$$

The concentrations of molecules, involved in a-convertons, b- convertons and Macroconvertons or c-Macrotransitons (see Introduction) are correspondingly:

$$N_M^{ac} = \frac{N_0}{Z^2 V_0} P_{ac}; \qquad N_M^{bc} = \frac{N_0}{Z^2 V_0} P_{bc}; \qquad N_M^C = \frac{N_0}{Z^4 V_0} P_{\text{cMt}} \tag{9.18}$$

The probabilities of convertons-related excitations are the same as used in Section 4.

The concentration of molecules, participating in the independent supereffectons and superdeformons:

$$N_M^{A^*} = \frac{N_0}{Z^4 V_0} P_s^{A^*}; \qquad N_M^{B^*} = \frac{N_0}{Z^4 V_0} P_S^{B^*} \tag{9.19}$$

$$N_M^{D^*} = \frac{N_0}{Z^8 V_0} P_S^{D^*} \tag{9.20}$$

where N_0 and V_0 are the Avogadro number and the molar volume of the matter.

Substituting (9.17 - 9.20) into well known Raleigh formula for scattering coefficient, measured at the right angle between incident and scattered beams:

$$R = \frac{I}{I_0} \frac{r^2}{V} = \frac{8\pi^4}{\lambda^4} \alpha^2 n_{\text{M}} \ (cm^{-1}) \tag{9.20a}$$

we obtain the values of contributions from different collective excitations: [tr] and [lb] macroeffectons in A and B states, macrodeformons and corresponding parameters of superdeformons - to the resulting scattering coefficient:

$$\left(R_A^M\right)_{tr,lb} = \frac{8\pi^4}{\lambda^4}\frac{(\alpha^*)^2}{Z^2}\frac{N_0}{V_0}\left(\ P_M^A\ \right)_{tr,lb};\quad R_A^s = \frac{8\pi^4}{\lambda^4}\frac{(\alpha^*)^2}{Z^4}\frac{N_0}{V_0}P_s^{A^*} \tag{9.21}$$

$$\left(R_B^M\right)_{tr,lb} = \frac{8\pi^4}{\lambda^4}\frac{(\alpha^*)^2}{Z^2}\frac{N_0}{V_0}\left(\ P_M^B\ \right)_{tr,lb};\quad R_B^s = \frac{8\pi^4}{\lambda^4}\frac{(\alpha^*)^2}{Z^4}\frac{N_0}{V_0}P_s^{B^*} \tag{9.22}$$

$$\left(R_D^M\right)_{tr,lb} = \frac{8\pi^4}{\lambda^4}\frac{(\alpha^*)^2}{Z^2}\frac{N_0}{V_0}\left(P_D^B\right)_{tr,lb};\quad R_D^s = \frac{8\pi^4}{\lambda^4}\frac{(\alpha^*)^2}{Z^4}\frac{N_0}{V_0}P_s^{D^*} \tag{9.23}$$

The contributions of excitations, related to $[tr/lb]$ convertons are:

$$R_{ac} = \frac{8\pi^4}{\lambda^4}\frac{(\alpha^*)^2}{Z^2}\ \frac{N_0}{V_0}R_{bc} = \frac{8\pi^4}{\lambda^4}\frac{(\alpha^*)^2}{Z^2}\frac{N_0}{V_0}P_{bc} \tag{9.23a}$$

$$R_{\rm abc} = \frac{8\pi^4}{\lambda^4}\frac{(\alpha^*)^2}{Z^4}\frac{N_0}{V_0}P_{\rm cMt} \tag{9.23b}$$

where: α^* is the acting polarizability determined by eq.(8.24) and (8.25).

The resulting coefficient of the isotropic scattering ($R_{\rm iso}$) is defined as the sum of contributions (9.21-9.23) and is subdivided into three kinds of scattering: caused by translational quasiparticles, caused by librational quasiparticles and by the mixed type of quasiparticles:

$$\begin{aligned} R_{\rm iso} = {} & [R_A^M + R_B^M + R_D^M]_{tr} + [R_A^M + R_B^M + R_D^M]_{lb} + \\ & + [R_{ac} + R_{bc} + R_{\rm abc}] + [R_A^s + R_B^s + R_D^s] \end{aligned} \tag{9.24}$$

Total contribution, including all kind of convertons and Superexcitations are correspondingly:

$$R_C = R_{ac} + R_{bc} + R_{\rm abc} \quad \text{and} \quad R_S = R_A^s + R_B^s + R_D^s \tag{9.24a}$$

The polarizability of anisotropic molecules having no cubic symmetry is a tensor. In this case, total scattering (R) consists of scattering at density fluctuations ($R_{\rm iso}$) and scattering at fluctuations of the anisotropy $\left(R_{\rm an} = \frac{13\Delta}{6-7\Delta}R_{\rm iso}\right)$:

$$R = R_{\rm iso} + \frac{13\Delta}{6-7\Delta}R_{\rm iso} = R_{\rm iso}\ \frac{6+6\Delta}{6-7\Delta} = R_{\rm iso}K \tag{9.25}$$

where $\mathrm{R_{iso}}$ corresponds to *eq.*(9.24); Δ is the depolarization coefficient.

The factor:

$$\left(\frac{6+6\Delta}{6-7\Delta}\right) = K$$

was obtained by Cabanne and is called after him. In the case of isotropic molecules when $\Delta = 0$, the Cabanne factor is equal to 1.

The depolarization coefficient (Δ) could be determined experimentally as the ratio:

$$\Delta = I_x / I_z, \tag{9.26}$$

where I_x and I_z are two polarized components of the beam scattered at right angle with respect to each other in which the electric vector is directed parallel and perpendicular to the incident beam, respectively. For example, in water $\Delta = 0.09$ (Vuks, 1977).

According to the proposed theory of light scattering in liquids the central unshifted (like in gases) component of the Brillouin scattering spectrum, is caused by fluctuations of concentration and self-diffusion of molecules, participating in the convertons, macrodeformons (tr and lib) and superdeformons. The scattering coefficients of the central line (R_{centr}) and side lines ($2R_{\text{side}}$) in transparent condensed matter, as follows from (9.24) and (9.25), are equal correspondingly to:

$$R_{\text{cent}} = K\left[\left(\ R_D^M\ \right)_{tr} + \left(\ R_D^M\ \right)_{lb}\right] + K(R_C + R_S) \tag{9.27}$$

and

$$2R_{\text{side}} = \left(\ R_A^M + R_B^M\ \right)_{tr} + \left(\ R_A^M + R_A^M\ \right)_{lb} \tag{9.27a}$$

where K is the Cabanne factor.

The total coefficient of light scattering is:

$$R_t = R_{\text{cent}} + 2R_{\text{side}} \tag{9.28}$$

In accordance with our model the fluctuations of anisotropy (Cabanne factor) should be taken into account for calculations of the central component only. The orientations of molecules in composition of A and B states of Macroeffectons are correlated and their coherent oscillations are not accompanied by fluctuations of anisotropy of polarizability (see Fig.26).

The probabilities of the convertons, macrodeformons and superdeformons excitations in crystals are much lower than in liquids and hence, the central line in the Brillouin spectra of crystals is not usually observed.

The lateral lines in Brillouin spectra are caused by the scattering on the molecules forming (A) and (B) states of spatially independent macroeffectons, as it was mentioned above.

The polarizabilities of the molecules forming the independent macroeffectons, synchronized in $(\text{A})_{tr,lb}$ and $(B)_{tr,lb}$ states and dielectric properties of these states, differ from each other and from that of transition states (macrodeformons). Such short-living states should be considered as the non equilibrium ones.

In fact we must keep in mind, that static polarizabilities in the more stable ground A state of the macroeffectons are higher than in B state, because the energy of long-term Van der Waals interaction between molecules of the A state is bigger than that of B-state.

If this difference may be attributed mainly to the difference in the long-therm dispersion interaction, then from (8.33) we obtain:

$$E_B - E_A = V_B - V_A = -\frac{3}{2}\frac{E_0}{r^6}\left(\ \alpha_B^2 - \alpha_A^2\ \right) \tag{9.29}$$

where polarizability of molecules in A-state is higher, than that in B-state:

$$\alpha_A^2 > \left[\left(\ \alpha^*\ \right)^2 \approx \alpha_D^2\right] > \alpha_B^2$$

The kinetic energy and dimensions of "acoustic" and "optic" states of macroeffectons are the same: $T_{\text{kin}}^A = T_{\text{kin}}^B$.

In our present calculations of light scattering we ignore this difference (9.29) between polarizabilities of molecules in A and B states.

But it can be taken into account if we assume, that polarizabilities in (A) and (a), (B) and (b) states of primary effectons are like:

$$\alpha_A \simeq \alpha_a \simeq \alpha^*;\ \ \alpha_B \simeq \alpha_b$$

and the difference between the potential energy of (a) and (b) states is determined mainly by dispersion interaction (eq.9.28).

Experimental resulting polarizability ($\alpha^* \simeq \alpha_a$) can be expressed as:

$$\alpha_a = f_a\alpha_a + f_b\alpha_b + f_t\alpha \tag{9.29a}$$

where $\alpha_t \simeq \alpha$ is polarizability of molecules in the gas state (or transition state);

$$f_a = \frac{P_a}{P_a + P_b + P_t};\quad f_b = \frac{P_b}{P_a + P_b + P_t};$$
$$\text{and}\quad f_t = f_d = \frac{P_t}{P_a + P_b + P_t}$$

are the fractions of (a), (b) and transition (t) states (equal to 9.66) as far $P_t = P_d = P_a \cdot P_b$.

On the other hand from (1.33) at $r = const$ we have:

$$\Delta V_{\text{dis}}^{b\to a} = -\frac{3}{4}\frac{(2\alpha\Delta\alpha)}{r^6}\cdot I_0 \quad (r_a = r_b;\ \ I_0^a \simeq I_0^b) \text{ and}$$

$$\frac{\Delta V_{\text{dis}}^{b\to a}}{V^b} = \frac{h\nu_p}{h\nu_b} = \frac{\Delta\alpha_a}{\alpha}\ \text{ or }\ \Delta\alpha_a = \alpha_a\,\frac{\nu_p}{\nu_b} \tag{9.29b}$$

$$\alpha_b = \alpha_a - \Delta\alpha_a = \alpha_a(1 - \nu_p/\nu_b)$$

where: $\Delta\alpha_a$ is a change of each molecule polarizability as a result of the primary effecton energy changing: $E_b \rightarrow E_a + h\nu_p$ with photon radiation; ν_b is a frequency of primary effecton in (b)- state (eq.9.28).

Combining (9.29) and (9.29b) we derive for α_a and α_b of the molecules composing primary translational or librational effectons:

$$\alpha_a = \frac{f_t\alpha}{1 - \left(f_a + f_b + f_b\frac{\nu_p}{\nu_b}\right)} \tag{9.30}$$

$$\alpha_b = \alpha_a\left(1 - \frac{\nu_p}{\nu_b}\right) \tag{9.30a}$$

The calculations by means of (9.30) are approximate in the framework of our assumptions mentioned above. But they correctly reflect the tendencies of α_a and α_b changes with temperature.

The ratio of intensities or scattering coefficients for the central component to the lateral ones previously was described by Landau- Plachek formula (9.10). According to our mesoscopic theory this ratio can be calculated in another way leading from (9.27) and (9.28):

$$\frac{I_{\text{centr}}}{2I_{M-B}} = \frac{R_{\text{cent}}}{2R_{\text{side}}} \tag{9.30b}$$

Combining (9.30) and Landau- Plachek formula (9.10) it is possible to calculate the ratio (β_T/β_S) and (C_P/C_V) using our mesoscopic theory of light scattering.

9.4. Factors that determine the Brillouin line width

The known equation for Brillouin shift is (see 9.7):

$$\Delta\nu_{M-B} = \nu_0 = 2\frac{v_s}{\lambda}n\sin(\theta/2) \tag{9.31}$$

where: v_s is the hypersonic velocity; λ is the wavelength of incident light, n is the refraction index of matter, and θ - scattering angle.

The deviation from ν_0 that determines the Brillouin side line half width *may be expressed as the result of fluctuations of sound velocity* v_s *and* n related to A and B states of tr and lib macroeffectons:

$$\frac{\Delta\nu_0}{\nu_0} = \left(\frac{\Delta v_s}{v_s} + \frac{\Delta n}{n}\right) \tag{9.32}$$

$\Delta\nu_0$ is the most probable side line width, i.e. the true half width of Brillouin line. It can be expressed as:

$$\Delta\nu_0 = \Delta\nu_{\rm exp} - F\Delta\nu_{\rm inc}$$

where $\Delta\nu_{\rm exp}$ is the half width of the experimental line, $\Delta\nu_{\rm inc}$ - the half width of the incident line, F - the coefficient that takes into account apparatus effects.

Let us analyze the first and the second terms in the right part of (9.32) separately.

The v_s squared is equal to the ratio of the compressibility modulus (K) and density (ρ):

$$v_s^2 = K^2/\rho \tag{9.33}$$

Consequently, from (9.33) we have:

$$\frac{\Delta v_s}{v_s} = \frac{1}{2}\left(\frac{\Delta K}{K} - \frac{\Delta\rho}{\rho}\right) \tag{9.34}$$

In the case of independent fluctuations of K and ρ ::

$$\frac{\Delta v_s}{v_s} = \frac{1}{2}\left(\left|\frac{\Delta K}{K}\right| - \left|\frac{\Delta\rho}{\rho}\right|\right) \tag{9.35}$$

From our equation (8.14) we obtain for refraction index:

$$n^2 = \left(1 - \frac{4}{3}N\alpha^*\right)^{-1}, \tag{9.36}$$

where $N = N_0/V_0$ is the concentration of molecules.

From (9.36) we can derive:

$$\frac{\Delta n}{n} = \frac{1}{2}\left(n^2 - 1\right)\left(\frac{\Delta\alpha^*}{\alpha^*} + \frac{\Delta N}{N}\right) \tag{9.37}$$

where:

$$(\Delta N/N) = (\Delta\rho/\rho) \tag{2.38}$$

and

$$\left(\frac{\Delta\alpha^*}{\alpha^*}\right) \simeq \left(\frac{\Delta K}{K}\right) \tag{9.39}$$

we can assume eq.(9.39) as far both parameters: polarizability (α^*) and compressibility models (K) are related with the potential energy of intermolecular interaction.

For the other hand one can suppose that the following relation is true:

$$\frac{\Delta\alpha^*}{\alpha^*} \simeq \frac{\mid \bar{E}^a_{ef} - 3kT \mid}{3kT} = \frac{\Delta K}{K} \tag{9.40}$$

where: $\bar{E}^a_{ef}$ is the energy of the secondary effectons in (ā) state; $E_0 = 3kT$ is the energy of an "ideal" quasiparticle as a superposition of 3D standing waves.

The density fluctuations can be estimated as a result of the free volume (v_f) fluctuations (see 9.45):

$$\left(\frac{\Delta v_f}{v_f}\right)_{tr,lb} = \frac{1}{Z}\left(P^M_D\right)_{tr,lb} \simeq (\Delta N/N)_{tr,lb} \tag{9.41}$$

Now, putting (9.40) and (9.41) into (9.37) and (9.34) and then into (9.32), we obtain the semiempirical formulae for the Brillouin line half width calculation:

$$\frac{\Delta\nu_f}{\nu_f} \simeq \frac{n^2}{2}\left[\frac{\mid \bar{E}^a_{ef} - 3kT \mid}{3kT} + \frac{1}{Z}\left(\ P^M_D\ \right)\right]_{tr,lb} \tag{9.42}$$

Brillouin line intensity depends on the half-width $\Delta\nu$ of the line in following ways:

for a Gaussian line shape:

$$I(\nu) = I_0^{\max} \exp\left[-0.693\left(\frac{\nu - \nu_0}{\frac{1}{2}\Delta\nu_0}\right)^2\right]; \tag{9.43}$$

for a Lorenzian line shape:

$$I(\nu) = \frac{I_0^{\max}}{1 + \left[\ (\nu - \nu_0)/\frac{1}{2}\Delta\nu_0\ \right]^2} \tag{9.44}$$

The traditional theory of Brillouin line shape gives a possibility for calculation of $\Delta\nu_0$ taking into account the elastic (acoustic) wave dissipation.

The fading out of acoustic wave amplitude may be expressed as:

$$A = A_0 e^{-\alpha x} \quad \text{or} \quad A = A_0 e^{-\alpha v_s} \tag{9.45}$$

where α is the extinction coefficient; $x = v_s t$ - the distance from the source of waves; v_s and t - sound velocity and time, correspondingly.

The hydrodynamic theory of sound propagation in liquids leads to the following expression for the extinction coefficient:

$$\alpha = \alpha_s + \alpha_b = \frac{\Omega^2}{2\rho v_s^3}\left(\frac{4}{3}\eta_s + \eta_b\right) \tag{9.46}$$

where: α_s and α_b are contributions to α, related to share viscosity (η_s) and bulk viscosity (η_b), respectively; $\Omega = 2\pi f$ is the angular frequency of acoustic waves.

When the side lines in Brillouin spectra broaden slightly, the following relation between their intensity (I) and shift ($\Delta\omega =\mid \omega - \omega_0 \mid$) from frequency ω_0, corresponding to maximum intensity ($I = I_0$) of side line is correct:

$$I = \frac{I_0}{1 + \left(\frac{\omega-\omega_0}{a}\right)}, \tag{9.47}$$

where:

$$a = \alpha v_s.$$

One can see from (9.46) that at $I(\omega) = I_0/2$, the half width:

$$\Delta\omega_{1/2} = 2\pi\Delta\nu_{1/2} = \alpha v_s \quad \text{and} \quad \Delta\nu_{1/2} = \frac{1}{2}\pi\alpha v_s \tag{9.48}$$

It will be shown in Chapter 12 how one can calculate the values of η_s and consequently α_s on the basis of the mesoscopic theory of viscosity.

9.5. Quantitative verification of hierarchic theory of Brillouin scattering

The calculations made according to the formula (9.21 - 9.27) are presented in Fig.26-28. The proposed theory of scattering in liquids, based on our hierarchic concept, is more adequate than the traditional Einstein, Brillouin, Landau-Plachek theories based on classical thermodynamics. It describes experimental temperature dependencies and the $I_{\text{centr}}/2I_{M-B}$ ratio for water very well (Fig.28).

The calculations are made for the wavelength of incident light: $\lambda_{ph} = 546.1nm = 5.461 \cdot 10^{-5}cm$. The experimental temperature dependence for the refraction index (n) at this wavelength was taken from the Frontas'ev and Schreiber paper (1965). The rest of data for calculating of various light scattering parameters of water (density the location of translational and librational bands in the oscillatory spectra) are identical to those used above in Chapter 6.

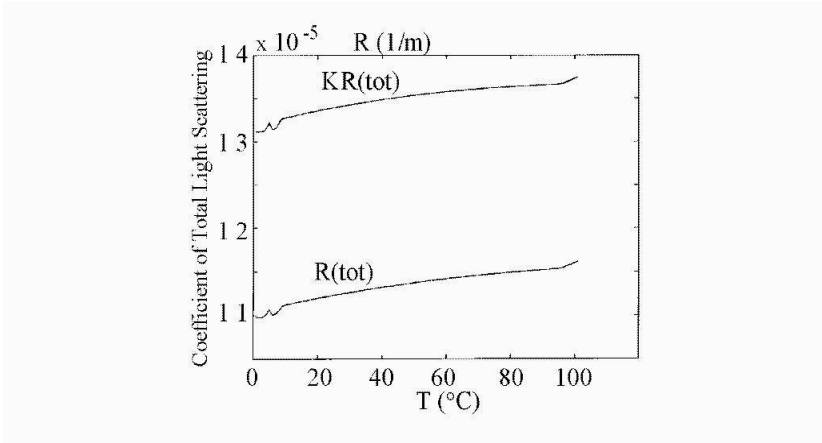

Fig. 26. Theoretical temperature dependencies of the total scattering coefficient for water without taking into account the anisotropy of water molecules polarizability fluctuations in the volume of macroeffectons, responsible for side lines: $[R(tot)]$ - eq.(9.27a; 9.28) and taking them into account: $[KR(tot)]$, where K is the Cabanne factor (eq.9.25).

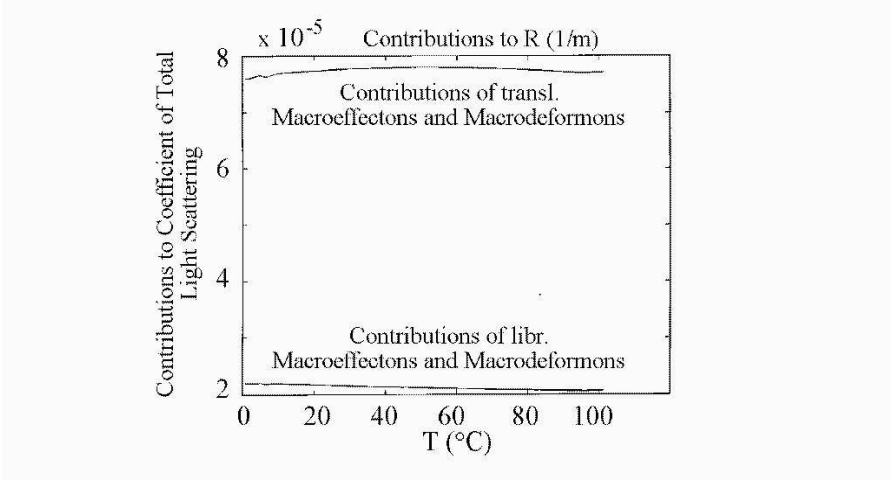

Fig. 27. Theoretical temperature dependencies of contributions to the total coefficient of total light scattering (R) caused by translational and librational macroeffectons and macrodeformons (without taking into account fluctuations of anisotropy).

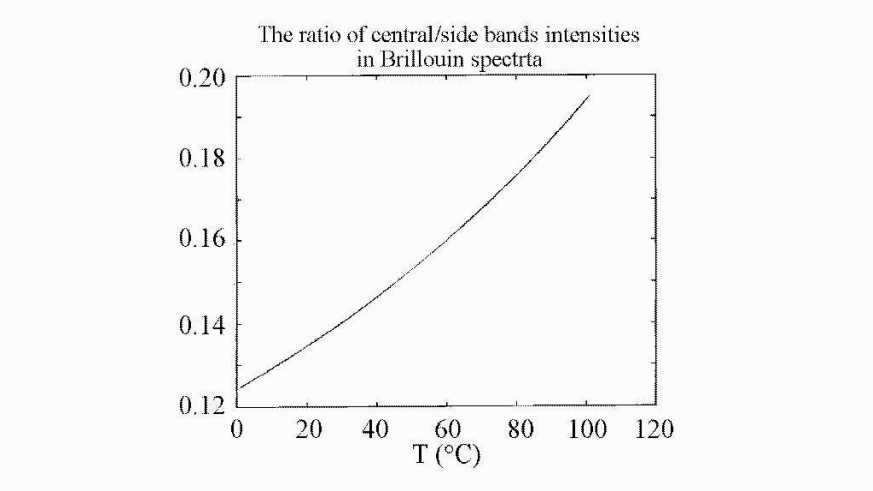

Fig. 28. Theoretical temperature dependencies of central to side bands intensities ratio in Brillouin spectra (eq.9.30).

Mesoscopic theory of light scattering can be used to verify the correctness of our formula for refraction index of condensed matter we got from our theory (eq. 1.14):

$$\frac{n^2-1}{n^2} = \frac{4}{3}\pi\frac{N_0}{V_0}\alpha^* \tag{9.48a}$$

and to compare the results of its using with that of the Lorentz-Lorenz formula:

$$\frac{n^2-1}{n^2+1} = \frac{4}{3}\pi\frac{N_0}{V_0}\alpha \tag{9.49}$$

From formula (9.48a) the resulting or effective molecular polarizability squared $(\alpha^*)^2$ used in eq.(9.21-9.23) is:

$$(\alpha^*)^2 = \left[\frac{(n^2-1)/n^2}{(4/3)\pi(N_0/V_0)}\right]^2 \tag{9.50}$$

On the other hand, from the Lorentz-Lorenz formula (9.49) we have another value of polarizability:

$$\alpha^2 = \left[\frac{(n^2-1)/(n^2+2)}{(4/3)\pi(N_0/V_0)}\right]^2 \tag{9.51}$$

It is evident that the light scattering coefficients (eq.9.28), calculated using (9.50) and (9.51) taking refraction index: $n = 1.33$ should differ more than four times as far:

$$\frac{R(\alpha^*)}{R(\alpha)} = \frac{(\alpha^*)^2}{(\alpha)^2} = \frac{(n^2-1)/n^2}{(n^2-1)/(n^2+2)} = \left(\frac{n^2+2}{n^2}\right)^2 = 4.56 \qquad (9.52)$$

At 25^0 and $\lambda_{ph} = 546nm$ the theoretical magnitude of the scattering coefficient for water, calculated from our formulae (9.28) is equal (see Fig.26) to:

$$R = 11.2 \cdot 10^{-5} m^{-1} \qquad (9.53)$$

This result of our theory coincides well with the most reliable experimental value (Vuks, 1977):

$$R_{\text{exp}} = 10.8 \cdot 10^{-5} m^{-1}$$

Multiplication of the side bands contribution ($2R_{\text{side}}$) to Cabanne factor increases the calculated total scattering to about 25% and makes the correspondence with experiment worse. This fact confirms our assumption that fluctuations of anisotropy of polarizability in composition of A and B states of macroeffectons should be ignored in light scattering evaluation due to correlation of molecular dynamics in these states, in contrast to that of macrodeformons.

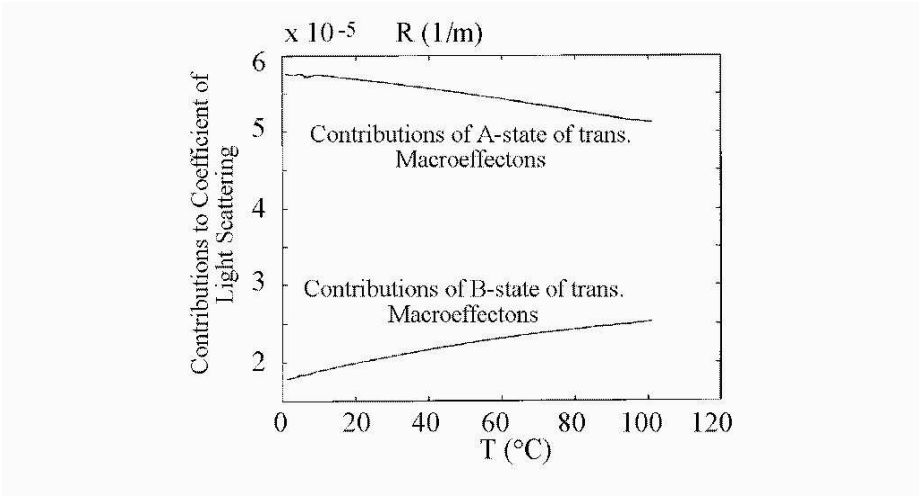

Fig. 29. Theoretical temperature dependencies of the contributions of A and B states of translational Macroeffectons to the total scattering coefficient of water (see also Fig.27);

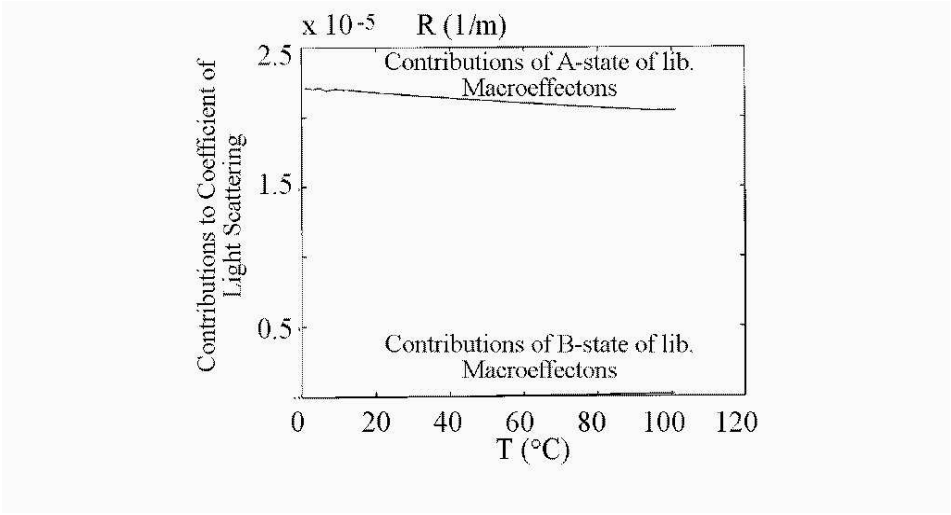

Fig. 30. Theoretical temperature dependencies of the contributions of the A and B states of librational Macroeffectons to the coefficient of light scattering (R).

It follows from the Fig.29 and Fig.30 that the light scattering depends on $(A \Leftrightarrow B)$ equilibrium of macroeffectons because $(R_A) > (R_B)$, i.e. scattering on A states is bigger than that on B states.

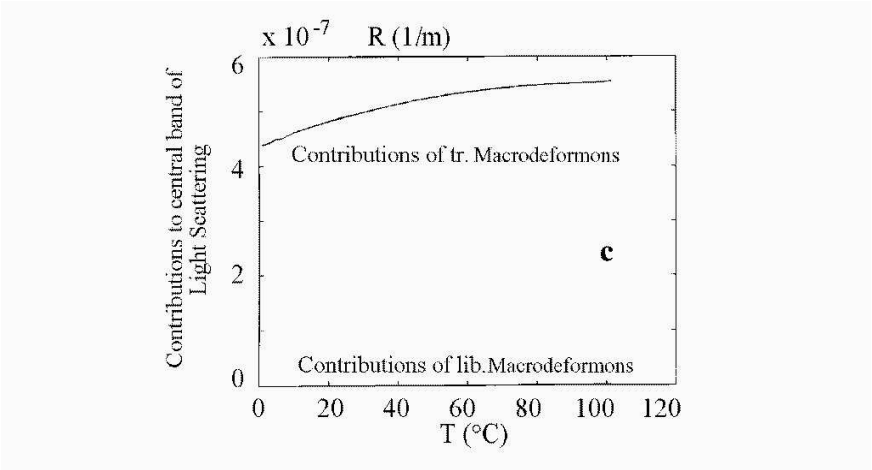

Fig. 31. Theoretical temperature dependencies of the contributions to light scattering (central component), related to translational $(R_D)_{tr}$ and librational $(R_D)_{lb}$ macrodeformons.

Comparing Figs. 26; 28, and 31 one can see that the main contribution to central component of light scattering is determined by $[lb/tr]$ convertons R_c (see eq.9.27).

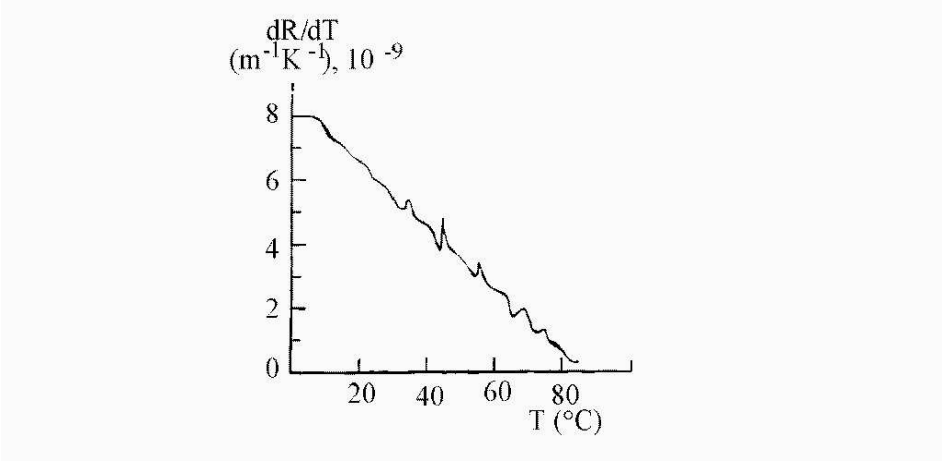

Fig. 32. Theoretical temperature dependences for temperature derivative (dR/dT) of the total coefficient of light scattering of water.

Nonmonotonic deviations of the dependencies dR/dT (Fig.32) reflect the nonmonotonic changes of the refraction index for water $n_{H_2O}(T)$, as indicated by available experimental data (Frontas'ev and Schreiber, 1965). The deviations of dependence $n_{H_2O}(t)$ from the monotonic way in accordance with hierarchic theory, are a consequence of the nonmonotonic change in the stability of water structure, i.e. nonlinear change of $(A \Leftrightarrow B)_{tr,lb}$ equilibrium. Some possible reasons of such equilibrium change were discussed in Chapter 6.

It is clear from (9.52) that the calculations based on the Lorentz-Lorentz formula (9.51) give scattering coefficient values of about 4.5 times smaller than experimental ones. It means that the true α^* value can be calculated only on the basis of our mesoscopic theory of light refraction (eq.9.50).

The traditional Smolukhovsky-Einstein theory, valid for the integral light scattering only (eq. 9.1), yield values in the range of $R = 8.85 \cdot 10^{-5}\, m^{-1}$ to $R = 10.5 \cdot 10^{-5}\, m^{-1}$ (Eisenberg, Kauzmann, 1969; Vuks, 1977).

The results, discussed above, demonstrate that new theory of light scattering works better and is more informative than the conventional one.

9.6. Light scattering in solutions

If the guest molecules are dissolved in a liquid and their sizes are much less than incident light wavelength, they do not radically alter the solvent properties. For this case the described above mechanism of light scattering of pure liquids does not changed qualitatively.

For such dilute solutions the scattering on the fluctuations of concentration of dissolved molecules (R_c) is simply added to the scattering on the density fluctuations of molecules of the host solvent (eq.9.28). Taking into account the fluctuations of molecule polarizability anisotropy (see 9.25) the total scattering coefficient of the solution (R_S) is:

$$R_S = R_t + R_c \tag{9.54}$$

Eqs. (9.21 - 9.28) could be used for calculating R_t until critical concentrations (C_{cr}) of dissolved substance when it start to destroy the solvent structure, so that the latter is no longer able to form primary librational effectons. Perturbations of solvent structure will induce low-frequency shift of librational bands in the oscillatory spectrum of the solution until these bands totally disappear.

If the experiment is made with a two-component solution of liquids, soluble in each other, e.g. water-alcohol, benzol-methanol etc., and the positions of translational and librational bands of solution components are different, then at the concentration of the dissolved substance: $C > C_{cr}$, the dissolved substance and the solvent (the guest and host) can switch their roles. Then the translational and librational bands pertinent to the guest subsystem start to dominate. In this case, R_t is to be calculated from the positions of the new bands corresponding to the "new" host-solvent. The total "melting" of the primary librational "host effectons" and the appearance of the dissolved substance "guest effectons" is *like the second order phase transition* and should be accompanied by a heat capacity jump. The like experimental effects take place indeed (Vuks, 1997).

According to our concept, the coefficient R_c in eq.(9.54) is caused by the fluctuations of concentration of dissolved molecules in the volume of translational and librational macro- and superdeformons of the solvent. If the destabilization of the solvent is expressed in the **low frequency** shift of librational bands, then the coefficients (R_A and $R_B)_{lb}$ increase (eq.9.21 and 9.22) with the probability of macro-excitations.. The probabilities of convertons and macro- and superdeformons and the central component of Brillouin spectra will increase also. Therefore, the intensity of the total light scattering increases correspondingly.

The fluctuations of concentration of the solute molecules, in accordance with our model, occur in the volumes of macrodeformons and superdeformons. Consequently, the contribution of solute molecules in scattering (R_c value in eq.9.54) can be expressed by formula, similar to (9.23), but containing the molecule polarizability of the dissolved substance ("guest"), equal to $(\alpha_g^*)^2$ instead of the molecule polarizability (α^*) of the solvent ("host"), and the molecular concentration of the "guest" substance in the solution (n_g) instead of the solvent molecule concentration ($n_M = N_0/V_0$). For this case R_c could be presented as a sum of the following contributions:

$$(R_c)_{tr,lb} = \frac{8\pi^4}{\lambda^4}(\alpha_g^*)^2 n_g \left[(P_M^D)_{tr,lb} + P_S^{D^*}\right] \tag{9.55}$$

$$R_c^{D^*} = \frac{8\pi^4}{\lambda^4}(\alpha_g^*)^2 n_g (P_S^{D^*}) \tag{9.55a}$$

The resulting scattering coefficient (R_e) on fluctuations of concentration in (9.54) is equal to:

$$R_c = (R_c)_{tr} + (R_c)_{lb} + R_c^{D^*} \tag{9.56}$$

If **a few** substances are dissolved with concentrations lower than (C_{cr}), then their R_c are summed up additively.

Formulae (9.55) and (9.56) are valid also for the dilute solutions.

Eqs.(9.21-9.28) and (9.54-9.56) should, therefore, be used for calculating the resulting coefficient of light scattering in solutions (R_S).

The traditional theory represents the scattering coefficient at fluctuations of concentration as (Vuks, 1977):

$$R_c = \frac{\pi^2}{2\lambda^4}\left(\frac{\partial\epsilon}{\partial x}\right)^2 \Delta x^2 v \tag{9.57}$$

where $(\partial\epsilon/\partial x)$ is the dielectric penetrability derivative with respect to one of the components: $\Delta\bar{x}^2$ is the fluctuations of concentration of guest molecules squared in the volume element v.

The transformation of (9.57) on the basis of classical thermodynamics (Vuks, 1977) leads to the formula:

$$R_c = \frac{\pi^2}{2\lambda^4 N_0}\left(2n\frac{\partial n}{\partial x}\right)\left(\frac{9n^2}{(2n^2+1)(n^2+2)}\right)^2 x_1 x_2 V_{12} f, \tag{9.58}$$

where N_0 is the Avogadro number, x_1 and x_2 are the molar fractions of the first and second components in the solution, V_{12} is the molar volume of the solution, f is the function of fluctuations of concentration determined experimentally from the partial vapor pressures of the first (P_1) and second (P_2) solution components:

$$\frac{1}{f} = \frac{x_1}{P_1}\frac{\partial P_1}{\partial x_1} = \frac{x_2}{P_2}\frac{\partial P_2}{\partial x_2} \tag{9.59}$$

In the case of ideal solutions

$$\frac{\partial P_1}{\partial x_1} = \frac{P_1}{x_1};\ \ \frac{\partial P_2}{\partial x_2} = \frac{P_2}{x_2}\ ;\ \text{and}\quad f = 1.$$

For application the mesoscopic theory of light scattering to study of crystals, liquids and solutions, the following information is needed:

1. Positions of translational and librational band maxima in oscillatory spectra;

2. Concentration of all types of molecules in solutions;

3. Refraction index or polarizability in the acting field of each component of solution at given temperature.

Application of our theory to quantitative analysis of transparent liquids and solids yields much more information about properties of matter, its mesoscopic and hierarchic dynamic structure than the traditional one.

10. Hierarchic theory of Mössbauer effect

10.1. General background

When the atomic nucleus with mass (M) in the gas phase irradiates γ-quantum with energy of

$$E_0 = h\nu_0 = m_p c^2 \tag{10.1}$$

where: m_p is the effective photon mass, then according to the law of impulse conservation, the nuclear acquires *additional* velocity in the opposite direction:

$$v = -\frac{E_0}{Mc} \tag{10.2}$$

The corresponding additional kinetic energy

$$E_R = \frac{Mv^2}{2} = \frac{E_0^2}{2Mc^2} \tag{10.3}$$

is termed **recoil energy.**

When an atom which irradiates γ-quantum is in composition of the solid body, then **three situations** are possible:

1. The recoil energy of the atom is higher than the energy of atom - lattice interaction. In this case, the atom irradiating γ-quantum would be knocked out from its position in the lattice. That leads to defects origination;

2. Recoil energy is insufficient for the appreciable displacement of an atom in the structure of the lattice, but is higher than the energy of phonon, equal to energy of secondary transitons and phonons excitation. In this case, recoil energy is spent for heating the lattice;

3. Recoil energy is lower than the energy of primary transitons, related to [emission/absorption] of IR translational and librational photons $(h\nu_p)_{tr,lb}$ and phonons $(h\nu_{ph})_{tr,lb}$. In that case, the probability (f) of γ-quantum irradiation without any the losses of energy appears, termed the probability (fraction) of a recoilless processes.

For example, when $E_R << h\nu_{ph}$ (ν_{ph} - the mean frequency of phonons), then the mean energy of recoil:

$$E_R = (1 - f)h\nu_{ph} \tag{10.4}$$

Hence, the probability of recoilless effect is

$$f = 1 - \frac{E_R}{h\nu_{ph}} \tag{10.5}$$

According to eq.(10.3) the decrease of the recoil energy E_R of an atom in the structure of the lattice is related to increase of its effective mass (M). In our model M corresponds to the mass of the effecton.

The effect of γ-quantum irradiation without recoil was discovered by Mössbauer in 1957 and named after him. The value of Mössbauer effect is determined by the value of $f \leq 1$.

The big recoil energy may be transferred to the lattice by portions that are **resonant** to the frequency of IR photons (tr and lb) and phonons. **The possibility of stimulation of superradiation of IR quanta as a result of such recoil process is a consequence of our model.**

The scattering of γ-quanta without lattice excitation, when $E_R << h\nu_{ph}$, is termed the *elastic* one. The general expression (Wertheim, 1964; Shpinel, 1969) for the probability of such phononless elastic γ-quantum radiation acts is equal to:

$$f = \exp\left(-\frac{4\pi < x^2 >}{\lambda_0^2}\right) \tag{10.6}$$

where $\lambda_0 = c/\nu_0$ is the real wavelength of γ-quantum; $<x^2>$ - the nucleus oscillations mean amplitude squared in the direction of γ-quantum irradiation.

The γ-quanta wavelength parameter may be introduced like:

$$L_0 = \lambda_0/2\pi, \tag{10.7}$$

where: $L_0 = 1.37 \cdot 10^{-5} cm$ for Fe^{57}, then eq.(10.6) could be written as follows:

$$f = \exp\left(-\frac{< x^2 >}{L_0^2}\right) \tag{10.8}$$

It may be shown (Shpinel, 1969), proceeding from the model of crystal as a system of 3N identical quantum oscillators, that when temperature (T) is much lower than the Debye one (θ_D) then:

$$< x^2 >= \frac{9\hbar^2}{4Mk\theta_D}\left\{1 + \frac{2\hbar^2 T^2}{3\theta_D^2}\right\}, \tag{10.9}$$

where $\theta_D = h\nu_D/k$ and ν_D is the Debye frequency.

From (10.1), (10.3) and (10.7) we have:

$$\frac{1}{L} = \frac{E_0}{\hbar c} \tag{10.10}$$

where: $E_0 = h\nu = c(2ME_R)^{1/2}$ is the energy of γ-quantum

Substituting eqs.(10.9 and 10.10) into eq.(10.8), we obtain the Debye-Valler formula:

$$f = \exp\left[-\frac{E_R}{k\theta_D}\left\{\frac{3}{2} + \frac{\pi^2 T^2}{\theta_D}\right\}\right] \tag{10.11}$$

when $T \to 0$, then

$$f \to \exp\left(-\frac{3E_R}{2k\theta_D}\right) \tag{10.12}$$

10.2. Probability of elastic effects

Mean square displacements $<x^2>$ of an atoms or molecules in condensed matter (eq. 10.8) is not related to excitation of thermal photons or phonons (i.e. primary or secondary transitons). According to our concept, $< x^2 >$ is caused by the mobility of the atoms forming effectons and differs for primary and secondary translational and librational effectons in $(a, \bar{a})_{tr,lb}$ and $(b, b)_{tr,lb}$ states.

We will ignore below the contributions of macro- and supereffectons in Mössbauer effect as very small. Then the resulting probability of elastic effects at γ-quantum radiation is determined by the sum of the following contributions:

$$f = \frac{1}{Z}\sum_{tr,lb}\left[\left(\ P^a_{ef} f^a_{ef} + P^b_{ef} f^b_{ef}\ \right) + \left(\ \bar{P}^a_{ef} \bar{f}^a_{ef} + \bar{P}^b_{ef} \bar{f}^b_{ef}\ \right)\right]_{tr,lb} \tag{10.13}$$

where: $P^a_{ef},\ P^b_{ef},\ \bar{P}^a_{ef},\ \bar{P}^b_{ef}$ are the relative probabilities of the *acoustic and optic* states for primary and secondary effectons; Z is the total partition function (see 4.10-4.19 and 4.2).

These parameters are calculated as described in Section 4 of this article. Each of contributions to resulting probability of the elastic effect can be calculated separately as:

$$\left(\ f^a_{ef}\ \right)_{tr,lb} = \exp\left[-\frac{<\left(\ x^a\ \right)^2_{tr,lb}>}{L_0^2}\right] \tag{10.14}$$

$\left(\ f^a_{ef}\ \right)_{tr,lb}$ is the probability of elastic effect, related to dynamics of primary translational and librational effectons in a-state;

$$\left(\ f^b_{ef}\ \right)_{tr,lb} = \exp\left[-\frac{<\left(\ x^b\ \right)^2_{tr,lb}>}{L_0^2}\right] \tag{10.15}$$

$\left(\ f^b_{ef}\ \right)_{tr,lb}$ is the probability of elastic effect in primary translational and librational effectons in b-state;

$$\left(\ \bar{f}^a_{ef}\ \right)_{tr,lb} = \exp\left[\ -\frac{<\left(\ \bar{x}^a\ \right)^2_{tr,lb}>}{L_0^2}\ \right] \tag{10.16}$$

$\left(\ \bar{f}^a_{ef}\ \right)_{tr,lb}$ is the probability for secondary effectons in $\bar{a}$ -state;

$$\left(\ \bar{f}^b_{ef}\ \right)_{tr,lb} = \exp\left[-\frac{<\left(\ \bar{x}^b\ \right)^2_{tr,lb}>}{L_0^2}\right] \tag{10.17}$$

$\left(\ \bar{f}^b_{ef}\ \right)_{tr,lb}$ is the probability of elastic effect, related to secondary effectons in $\bar{b}$-state.

Mean square displacements within different types of effectons in eqs.(10.14-10.17) are related to their phase and group velocities. At first we express the displacements using group velocities of the waves B (v_{gr}) and periods of corresponding oscillations (T) as:

$$<\left(\ x^a\ \right)^2_{tr,lb}>=\frac{<(v^a_{gr})^2_{tr,lb}>}{<\nu_a^2>_{tr,lb}}=<\left(\ v^a_{gr}T^a\ \right)^2_{tr,lb}> \tag{10.18}$$

where $(T^a)_{tr,lb}=(1/\nu_a)_{tr,lb}$ is a relation between the period and the frequency of primary translational and librational effectons in a-state;

$(v^a_{gr}=v^b_{gr})_{tr,lb}$ are the group velocities of atoms forming these effectons equal in (a) and (b) states.

In a similar way we can express the displacements of atoms forming (b) state of primary effectons (tr and lib):

$$<\left(\ x^b\ \right)^2_{tr,lb}>=\frac{<(v^b_{gr})^2_{tr,lb}>}{<\nu_b^2>_{tr,lb}} \tag{10.19}$$

where ν_b is the frequency of *primary* translational and librational effectons in b-state.

The mean square displacements of atoms forming *secondary* translational and librational effectons in $\bar{a}$ and $\bar{b}$ states:

$$<\left(\ \bar{x}^a\ \right)^2_{tr,lb}>=\frac{<(\overline{v}^a_{gr})^2_{tr,lb}>}{<\bar{\nu}_a^2>_{tr,lb}} \tag{10.20}$$

$$<\left(\ \bar{x}^b\ \right)^2_{tr,lb}>=\frac{<(\overline{v}^b_{gr})^2_{tr,lb}>}{<\bar{\nu}_b^2>_{tr,lb}} \tag{10.21}$$

where: $(\bar{v}^a_{gr}=\bar{v}^b_{gr})_{tr,lb}$

Group velocities of atoms in primary and secondary effectons may be expressed using corresponding phase velocities (v_{ph}) and formulae for waves B length as follows:

$$\left(\ \lambda_a\ \right)_{tr,lb}=\frac{h}{m<v_{gr}>_{tr,lb}}=\left(\frac{v^a_{ph}}{\nu_a}\right)_{tr,lb}= \tag{10.22}$$

$$=\left(\ \lambda_b\ \right)_{tr,lb}=\left(\frac{v^b_{ph}}{\nu_b}\right)_{tr,lb}$$

hence for the group velocities of the atoms or molecules forming primary effectons (*tr and lb*) squared we have:

$$\left(\ v_{gr}^{a,b}\ \right)_{tr,lb}^{2} = \frac{h^2}{m^2}\left(\frac{\nu_{a,b}}{v_{ph}^{a,b}}\right)_{tr,lb}^{2} \tag{10.23}$$

In accordance with mesoscopic theory, the wave B length, impulses and group velocities in a and b states of the effectons are equal. Similarly to (10.23), we obtain the group velocities of particles, composing secondary effectons:

$$\left(\ \bar{v}_{gr}^{a,b}\ \right)_{tr,lb}^{2} = \frac{h^2}{m^2}\left(\frac{\bar{\nu}_{a,b}}{\bar{v}_{ph}^{a,b}}\right)_{tr,lb}^{2} \tag{10.24}$$

Substituting eqs.(10.23) and (10.24) into (10.18-10.21), we find the important expressions for the average coherent displacements of particles squared as a result of their oscillations in the volume of the effectons (*tr, lib)* in both discreet states (acoustic and optic):

$$< (x^a)_{tr,lb}^2 >= (h/mv_{ph}^a)_{tr,lb}^2 \tag{10.25}$$

$$< (x^b)_{tr,lb}^2 >= (h/mv_{ph}^b)_{tr,lb}^2 \tag{10.26}$$

$$< (\overline{x}^a)_{tr,lb}^2 >= (h/m\overline{v}_{ph}^a)_{tr,lb}^2 \tag{10.27}$$

$$< (\overline{x}^b)_{tr,lb}^2 >= (h/m\overline{v}_{ph}^b)_{tr,lb}^2 \tag{10.28}$$

Then, substituting these values into eqs.(10.14-10.17) we obtain a set of different contributions to the resulting probability of effects without recoil:

$$\left.\begin{array}{l} \left(\ f_f^a\ \right)_{tr.lb} = \exp\left[-\left(\frac{h}{mL_0 v_{ph}^a}\right)^2\right]_{tr,lb}; \\ \left(\ f_f^b\ \right)_{tr.lb} = \exp\left[-\left(\frac{h}{mL_0 v_{ph}^b}\right)^2\right]_{tr,lb}; \end{array}\right\} \tag{10.29}$$

$$\left.\begin{array}{l} \left(\ \bar{f}_f^a\ \right)_{tr.lb} = \exp\left[-\left(\frac{h}{mL_0 \bar{v}_{ph}^a}\right)^2\right]_{tr,lb}; \\ \left(\ \bar{f}_f^b\ \right)_{tr.lb} = \exp\left[-\left(\frac{h}{mL_0 \bar{v}_{ph}^b}\right)^2\right]_{tr,lb}; \end{array}\right\} \tag{10.30}$$

where the phase velocities $(v_{ph}^a,\ v_{ph}^b,\ \bar{v}_{ph}^a,\ \bar{v}_{ph}^b)_{tr,lb}$ are calculated from the resulting sound velocity and the positions of translational and librational bands in the oscillatory spectra of matter at given temperature using eqs.2.69-2.75. The wavelength parameter:

$$L_0 = \frac{c}{2\pi\nu_0} = \frac{hc}{2\pi E_0} = 1.375 \cdot 10^{-11}\, m$$

for gamma-quanta, radiated by nuclear of Fe^{57}, with energy:

$$E_0 = 14.4125 \text{ kev } = 2.30167 \cdot 10^{-8} \text{ erg}$$

Substituting eqs.(10.29) and (10.30) into (10.13), we find the total probability of recoilless effects (f_{tot}) in the given substance. Corresponding computer calculations for ice and water are presented on Figs.33 and 34.

As far the second order phase transitions in general case are accompanied by the alterations of the sound velocity and the positions of translational and librational bands, they should also be accompanied by alterations of f_{tot} and its components.

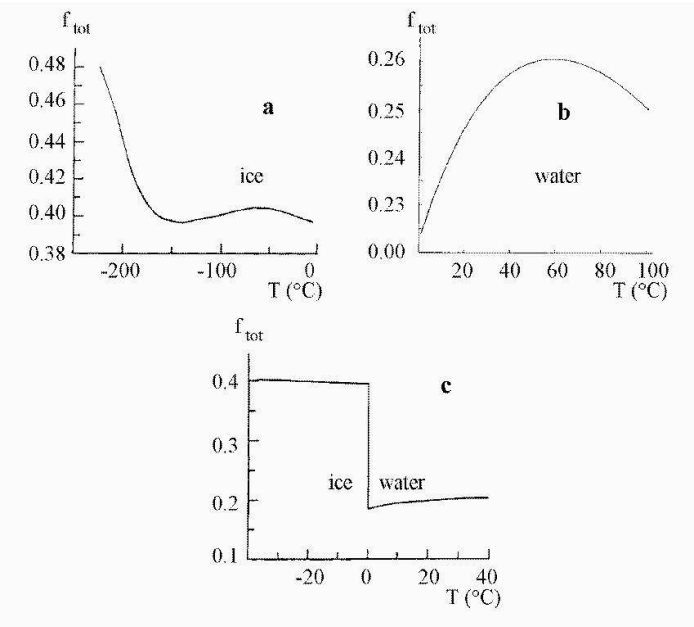

Fig. 33. Temperature dependences of total probability (f) for elastic effect without recoil and phonon excitation: (a) in ice; (b) in water; (c)-during phase transition. The calculations were performed using eq.(10.13).

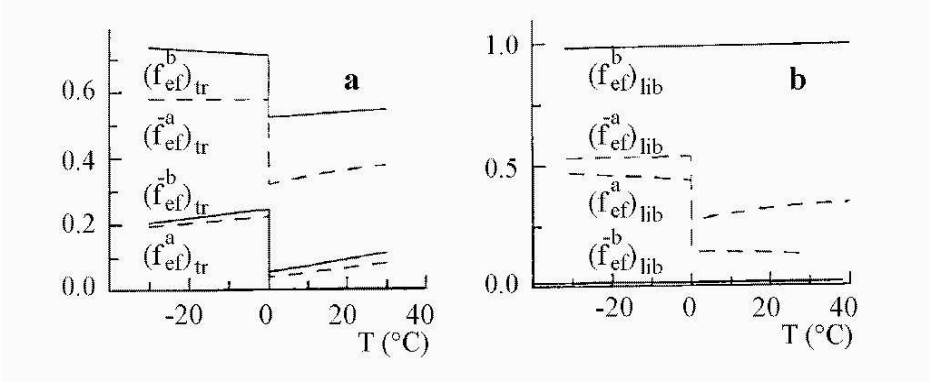

Fig. 34(**a**) - The contributions to probability of elastic effect (f), presented at Fig.33, related to primary $(f^{a,b}_{ef})_{tr}$ and secondary $(\bar{f})_{tr}$ translational effectons; **(b)** - contributions, related to primary $(f^{a,b}_{ef})_{lb}$ and secondary $(\bar{f})_{lb}$ librational effectons around the temperature of [ice $\Leftrightarrow$ water] phase transition.

The total probability (f) and its components, caused by primary and secondary quasiparticles were calculated according to formula (10.13). The value of (f) determines the magnitude of the Mössbauer effect registered by γ-resonance spectroscopy.

The band width caused by recoilless effects is determined by the uncertainty principle and expressed as follows:

$$\Gamma = \frac{h}{\tau} \approx \frac{10^{-27}}{1.4 \cdot 10^{-7}} = 7.14 \cdot 10^{-21} \text{ erg } = 4.4 \cdot 10^{-9} eV \qquad (10.31)$$

where τ is the lifetime of nucleus in excited state (for Fe^{57} $\tau = 1.4 \cdot 10^{-7} s$).

The position of the band depends on the mean square velocity of atoms, i.e. on second order Doppler effect. In the experiment, such an effect is compensated by the *velocity of γ-quanta source* motion relative to absorbent. In the framework of our model this velocity is interrelated with the mean velocity of the secondary effectons diffusion in condensed matter.

10.3. Doppler broadening in spectra of nuclear gamma-resonance (NGR)

Mössbauer effect is characterized by the unbroadened component of NGR spectra only, with probability of observation determined by eq.(10.13).

When the energy of absorbed γ-quanta exceeds the energy of thermal IR *photons (tr,lib)* or *phonons excitation,* the absorbance band broadens as a result of Doppler effect. Within the framework of our mesoscopic concept the Doppler broadening is caused by thermal displacements of the particles during $[a \Leftrightarrow b$ and $\bar{a} \Leftrightarrow \bar{b}]_{tr,lb}$ transitions of primary and secondary effectons, leading to origination/annihilation of the corresponding type of deformons (electromagnetic and acoustic).

The *flickering clusters*: $[lb/tr]$ convertons (a and b), can contribute in the NGR line broadening also.

In that case, the value of Doppler broadening ($\Delta\Gamma$) of the band in the NGR spectrum could be estimated from corresponding kinetic energies of these excitations, related to their group velocities (see eq. 4.31). In our consideration we take into account the **reduced to one molecule** kinetic energies of primary and secondary translational and librational transitons, a-convertons and b-convertons. The contributions of macroconvertons, macro- and superdeformons are much smaller due to their small probability and concentration:

$$\Delta\Gamma = \frac{V_0}{N_0 Z}\sum_{tr,lb}\left(\ n_t P_t T_t + \bar{n}_t \bar{P}_t \bar{T}_t\ \right)_{tr,lb} + \tag{10.32}$$
$$+ \frac{V_0}{N_0 Z}(n_{ef})_{lb}[P_{ac}T_{ac} + P_{bc}T_{bc}]$$

where: N_0 and V_0 are the Avogadro number and molar volume;

Z is the total partition function (eq.4.2); n_t and $\bar{n}_t$ are the concentrations of primary and secondary transitons (eqs.10.5 and 10.7);

$(n_{ef})_{lb} = n_{\rm con}$ is a concentration of primary librational effectons, equal to that of the convertons; P_t and $\bar{P}_t$ are the relative probabilities of primary and secondary transitons (eqs. 4.26 and 4.27); P_{ac} and P_{bc} are relative probabilities of (a and b) -convertons (see section 4);

T_t and $\bar{T}_t$ are the kinetic energies of primary and secondary transitons, related to the corresponding total energies of these excitations (E_t and $\bar{E}_t$), their masses (M_t and $\overline{M}_t$) and the resulting sound velocity (v_s, see eq.2.40) in the following form:

$$(T_t)_{tr,lb} = \frac{\sum_1^3 \left(E_t^{1,2,3}\right)_{tr,lb}}{2M_t(v_s^{\rm res})^2} \tag{10.33}$$

$$(T_t)_{tr,lb} = \frac{\sum_1^3 \left(\bar{E}_t^{1,2,3}\right)_{tr,lb}}{2\bar{M}_t(v_s^{\rm res})^2} \tag{10.34}$$

The kinetic energies of (a and b) convertons are expressed in a similar way:

$$(T_{ac}) = \frac{\sum_1^3 \left(E_{ac}^{1,2,3}\right)_{tr,lb}}{2M_c(v_s^{\rm res})^2} \tag{10.34a}$$

$$(T_{bc}) = \frac{\sum_1^3 \left(E_{bc}^{1,2,3}\right)_{tr,lb}}{2M_c(v_s^{\rm res})^2} \tag{10.34b}$$

where: $E_{ac}^{1,2,3}$ and $E_{bc}^{1,2,3}$ are the energies of selected states of corresponding convertons; M_c is the mass of convertons, equal to that of primary librational effectons.

The broadening of NGR spectral lines by Doppler effect in liquids is generally expressed using the diffusion coefficient (D) at the assumption that the motion of Mössbauer atom has the character of unlimited diffusion (Singvi, 1962):

$$\Delta\Gamma = \frac{2E_0^2}{\hbar c^2} D \tag{10.35}$$

where: $E_0 = h\nu_0$ is the energy of gamma quanta; c is light velocity and

$$D = \frac{kT}{6\pi\eta a} \tag{10.36}$$

where: η is viscosity, (a) is the effective Stokes radius of the atom Fe^{57}

The probability of recoilless γ-quantum absorption by the matter containing for example Fe^{57}, decreases due to diffusion and corresponding Doppler broadening of band ($\Delta\Gamma$):

$$f_D = \frac{\Gamma}{\Gamma + \Delta\Gamma} \tag{10.37}$$

where $\Delta\Gamma$ corresponds to eq.(10.32).The formulae obtained here make it possible to experimentally verify a set of consequences of our mesoscopic theory using the gamma- resonance method. A more detailed interpretation of the data obtained by this method also becomes possible.

The magnitude of ($\Delta\Gamma$) was calculated according to formula (10.32). It corresponds well to experimentally determined Doppler widening in the nuclear gamma resonance (NGR) spectra of ice.

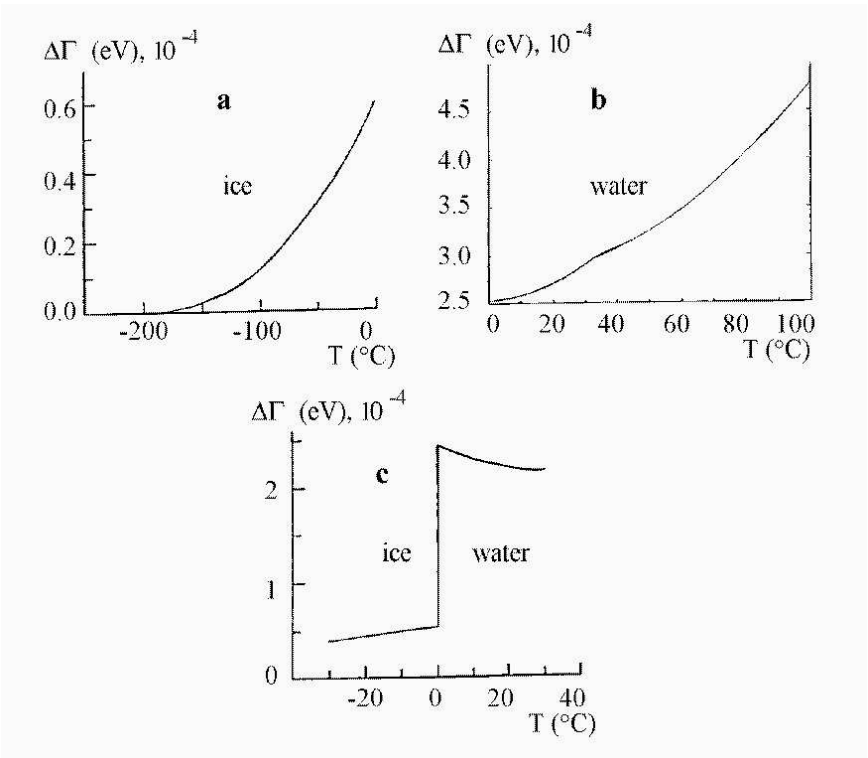

Fig. 35. The temperature dependences of the parameter $\Delta\Gamma$, characterizing the nonelastic effects and related to the excitation of thermal phonons and IR photons: **a**) in ice; **b**) in water; **c**) near phase transition.

10.4. Acceleration and forces, related to thermal dynamics of molecules and ions. Vibro-Gravitational interaction.

During the period of particles thermal oscillations (tr and lb), their instant velocity, acceleration and corresponding forces alternatively and strongly change.

The change of wave B instant group velocity, averaged during the molecule oscillation period in composition of the (a) and (b) states of the effectons, determines the average *acceleration:*

$$\left[a_{gr}^{a,b} = \frac{dv_{gr}^{a,b}}{dt} = \frac{v_{gr}^{a,b}}{T} = v_{gr}\nu^{a,b}\right]_{tr,lb}^{1,2,3} \tag{10.38}$$

We keep in mind that group velocities, impulses and wave B length in (a) and (b) states of the effectons are equal, in accordance with our model.

Corresponding to (10.38) forces:

$$\left[F^{a,b} = ma_{gr}^{a,b}\right]_{tr,lb}^{1,2,3} \tag{10.39}$$

The energies of molecules in (a) and (b) states of the effectons also can be expressed via accelerations:

$$\left[E^{a,b} = h\nu^{a,b} = F^{a,b}\lambda = ma^{a,b}\cdot\lambda = ma^{a,b}(v_{ph}^{a,b}/\nu^{a,b})\right]_{tr,lb}^{1,2,3} \tag{10.40}$$

From (10.40) one can express the accelerations of particles in the primary effectons of condensed matter, using their phase velocities as a waves B:

$$\left[a_{gr}^{a,b} = \frac{h(\nu^{a,b})^2}{mv_{ph}^{a,b}}\right]_{tr,lb}^{1,2,3} \tag{10.41}$$

The accelerations of particles in composition of secondary effectons have a similar form:

$$\left[\bar{a}_{gr}^{a,b} = \frac{h(\bar{\nu}^{a,b})^2}{m\bar{v}_{ph}^{a,b}}\right]_{tr,lb}^{1,2,3} \tag{10.42}$$

These parameters are important for understanding the dynamic properties of condensed systems. The accelerations of the atoms, forming primary and secondary effectons can be calculated, using eqs.(3.35; 3.36) to determine phase velocities and eqs. (3.5; 3.6 and 3.16; 3.17) to find a frequencies.

Multiplying (10.41) and (10.42) by the atomic mass m, we derive the most probable and mean forces, acting upon the particles in both states of primary and secondary effectons in condensed matter:

$$\left[F_{gr}^{a,b} = \frac{h(\nu^{a,b})^2}{v_{ph}^{a,b}}\right]_{tr,lb}^{1,2,3} \qquad \left[\bar{F}_{gr}^{a,b} = \frac{h(\bar{\nu}^{a,b})^2}{\bar{v}_{ph}^{a,b}}\right] \tag{10.43}$$

The comparison of calculated accelerations with empirical data of the Mössbauer effect - supports the correctness of our approach.

According to eq.(3.5) in the low temperature range, when $h\nu_a << kT$, the frequency of *secondary tr and lb* effectons in the (a) state can be estimated as:

$$\nu^a = \frac{\nu_a}{\exp\left(\frac{h\nu_a}{kT}\right) - 1} \approx \frac{kT}{h} \tag{10.44}$$

For example, at $T = 200K$ we have $\bar{\nu}^a \approx 4 \cdot 10^{12} s^{-1}$.

If the phase velocity in eq.(10.42) is taken equal to $\bar{v}_{ph}^a = 2.1 \cdot 10^5 cm/s$ and the mass of water molecule:

$$m = 18 \cdot 1.66 \cdot 10^{-24} g = 2.98 \cdot 10^{-23} g,$$

then from (10.42) we get the acceleration of molecules in composition of secondary effectons of ice in (a) state:

$$\bar{a}_{gr}^a = \frac{h(\bar{\nu}^a)^2}{m\bar{v}_{ph}^a} = 1.6 \cdot 10^{16} cm/s^2 \tag{10.45}$$

This value is about 10^{13} times more than that of free fall acceleration ($g = 9.8 \cdot 10^2 cm/s^2$), which agrees well with experimental data, obtained for solid bodies (Wertheim, 1964).

Accelerations of H_2O molecules in composition of *primary librational* effectons (a_{gr}^a) in the ice at 200K and in water at 300K are equal to: $0.6 \cdot 10^{13} cm/s^2$ and $2 \cdot 10^{15} cm/s^2$, correspondingly. **They also exceed to many orders the free fall acceleration.**

It was shown experimentally (Sherwin, 1960), that heating of solid body leads to decreasing of gamma-quanta frequency (red Doppler shift) i.e. increasing of corresponding quantum transitions period. This can be explained as the relativist time-pace decreasing due to elevation of average thermal velocity of atoms.

The thermal vibrations of particles (atoms, molecules) in composition of primary effectons as a partial Bose-condensate are coherent. The increasing of such clusters dimensions, determined by most probable wave B length, as a result of cooling, pressure elevation or under magnetic field action leads to enhancement of coherent regions.

Each coherently vibrating cluster of particles with big alternating accelerations, like librational and translational effectons is a source of coherent gravitational waves.

The frequency of these vibro-gravitational waves (VGW) is equal to frequency of particles vibrations (i.e. frequency of the effectons in a or b states). The amplitude of VGW (A_G) is proportional to the number of vibrating coherently particles (N_G) in composition of primary effectons:

$$A_G \sim N_G \sim V_{ef}/(V_0/N_0) = (1/n_{ef})/(V_0/N_0) \tag{10.46}$$

The resonant long-distance gravitational interaction between coherent clusters of the same body or between that of different bodies is possible. The formal description of this vibro-gravitational interaction (VGI) could be like that of distant macroscopic Van der Waals interaction.

Different patterns of virtual Bose-condensate of standing gravitational waves in vacuum represent the vibro-gravitational replica (VGR) of condensed matter.

Important role of proposed here distant resonant VIBRO - GRAVITATIONAL INTERACTION (VGI) in elementary acts of perception and memory can be provided by coherent primary librational water effectons in microtubules of the nerve cells (see article: "Hierarchic Model of Consciousness" by Kaivarainen, 2000).

11. ENTROPY-INFORMATIONAL CONTENT OF MATTER, SLOW RELAXATION, MACROSCOPIC OSCILLATIONS. AND EFFECTS OF MAGNETIC FIELD

11.1. Theoretical background

One of the consequences of our concept is of special interest. It is the possibility for oscillation processes in solids and liquids. The law of energy conservation is not violated thereupon because the energies of two quasiparticle subsystems related to effectons and deformons, can change in opposite phases. The total internal energy of matter keeps almost constant.

The equilibrium shift between subsystems of condensed matter can be induced by any external factor, i.e. pressure or field. The relaxation time, necessary for system to restore its equilibrium, corresponding to minimum of potential or free energy after switching off external factor can be termed "memory" of system.

The energy redistribution between primary and secondary effecton and deformon subsystems may have a periodical character, coupled with the oscillation of the $(a \Leftrightarrow b)$ equilibrium constant of primary effectons ($K_{a\Leftrightarrow b}$) and correlated oscillations of primary electromagnetic deformons concentration if dissipation processes are weak or reversible. According to our model (Table 1) the $(a \rightarrow b)$ transition of primary effecton is related to photon absorption, i.e. a decrease in primary electromagnetic deformon concentration, while the $(b \rightarrow a)$ transition on the contrary, radiate photons. If, therefore, the $[a \Leftrightarrow b]$ and $\left[\bar{a} \Leftrightarrow \bar{b}\right]$ equilibriums are shifted right ward, and equilibrium constants $K_{a\Leftrightarrow b}$ and $\bar{K}_{a\Leftrightarrow b}$ decreases, then concentrations of primary and secondary deformons (n_d and $\bar{n}_d$) also decreases. If $K_{a\Leftrightarrow b}$ grows up, i.e. the concentration of primary effectons in a-states increases, then n_d increases. We remind that (**a**) and (**b**) states of the primary effectons correspond to the more and less stable molecular clusters

(see Introduction). In accordance with our model, the strong interrelation exists between dynamic equilibrium of primary and secondary effectons. Equilibrium of primary effectons is more sensitive to any perturbations. However, the equilibrium shift of secondary effectons affect the total internal energy, the entropy change and possible mass defect (see below) stronger than that of primary effectons.

As we have shown (Fig. 29, 30), the scattering ability of A-states is more than two times as high as that of B-states. Their polarizability, refraction index and dielectric permeability are also higher. It makes possible to register the oscillations in the condensed matter in different ways.

In accordance with our theory the oscillation of refraction index must induce the corresponding changes of viscosity and self-diffusion in condensed matter. The diffusion variations are possible, for example, in solutions of macromolecules or other Brownian particles. In such a way self-organization in space and time gradually may originate in appropriate solvents, solutions, colloid systems and even in solid bodies.

The period and amplitude of these oscillations depend on the times of relaxation processes which are related to the activation energy of equilibrium shifts in the effectons, polyeffectons or coherent superclusters of primary effectons subsystems.

The reorganizations in the subsystems of translational and librational effectons, macro- and supereffectons, as well as chain-like polyeffectons, whose stabilities and sizes differ from each other, must go on at different rates. It should, therefore, be expected that in the experiment the presence of several oscillation processes would be revealed. These processes are interrelated but going with different periods and amplitudes. Concomitant oscillations of self-diffusion rate also must be taken into account. In such a way Prigogin's dissipative structures could be developed (Prigogin, 1984). Instability in the degree of ordering in time and space is accompanied by the slow oscillation of entropy of the whole macroscopic system.

The coherent extraterrestrial cosmic factors and gravitational instabilities can induce long relaxation and oscillation processes in water and other kind of condensed matter (Udaltsova, et. al., 1987).

11.2. The entropy - information content of matter as a hierarchic system

The statistical weigh for macrosystem (P), equal to number of microstates (W), corresponding to given macrostate, necessary for entropy calculation could be presented as:

$$W = \frac{N!}{N_1! \cdot N_2! \cdot \ldots \cdot N_q!} \tag{11.1}$$

where:

$$N = N_1 + N_2 + ...N_q \tag{11.2}$$

is the total number of molecules in macrosystem;

N_i **is the number of molecules in the i-th state;**

q **is the number of independent states of all quasiparticles in macrosystem.**

We can subdivide macroscopic volume of $1cm^3$ into 24 types of quasiparticles in accordance with our hierarchic model (see Table 1).

In turn, each type of the effectons (primary, secondary, macro- and supereffectons) is subdivided on two states: ground (a,A) and excited (b,B) states. Taking into account two ways of the effectons origination - due to thermal translations (tr) and librations (lb), excitations, related to $[lb/tr]$ convertons, macro- and super deformons, the total number of **independent** states is 24 also. It is equal to number of independent relative probabilities of excitations, composing partition function Z (see eq.4.2). Consequently, we have:

$$q = 24$$

The **number** of molecules, in the unit of volume of condensed matter (1cm^3), participating in each of 24 excitation states (i) can be calculated as:

$$N_i = \frac{(v)_i}{V_0/N_0} \cdot n_i \cdot \frac{P_i}{Z} = \frac{N_0}{V_0}\frac{P_i}{Z} \tag{11.3}$$

where: $(v)_i = 1/n_i$ is the volume of (i) quasiparticle, equal to reciprocal value of its concentration (n_i); N_0 and V_0 are Avogadro number and molar volume, correspondingly; Z is partition function and P_i are relative probabilities of independent excitations in composition of Z (eq.4.2).

The total number of molecules of (i)-type of excitation in any big volume of matter (V_{Mac}) is equal to

$$N^i_{\text{Mac}} = N_i V_{\text{Mac}} = V_{\text{Mac}}\frac{N_0}{V_0}\frac{P_i}{Z} \tag{11.3a}$$

Now we can calculate the statistical weight and entropy from eqs.(11.1 and 11.4).

For large values of N_i it is convenient to use a Stirling formula:

$$N_i = (2\pi N)^{1/2}(N/e)^N \cdot \exp(\Theta/12N) \sim (2\pi N)^{1/2}(N/\Theta)^N \tag{11.3b}$$

Using this formula and (11.1), one can obtain the following expression for entropy:

$$S = k \cdot \ln W = -k \cdot \sum_i^q (N_i + \frac{1}{2}) \ln N_i + \text{ const } = S_1 + S_2 + ...S_i \tag{11.4}$$

From this eq. we can see that the temperature increasing or [solid $\rightarrow$ liquid] phase transition will lead to the entropy elevation:

$$\Delta S = S_L - S_S = k \cdot \ln(W_L/W_S) > 0 \tag{11.5}$$

It follows from (11.4) and (11.3) that under conditions when (P_i) and N_i undergoes oscillations it can lead to oscillations of contributions of different types of quasiparticles to the entropy of system and even to oscillations of total entropy of system as an additive parameter. The coherent oscillations of P_i and N_i can be induced by different external fields: acoustic, electromagnetic and gravitational. Macroscopic autooscillations may arise spontaneously also in the sensitive and highly cooperative systems.

Experimental evidence for such phenomena will be discussed in the next section.

The notions of probability of given microstate ($p_i = 1/W$), entropy (S_i) and information (I_i) are strongly interrelated. The smaller the probability the greater is information (Nicolis 1986):

$$I_i = \lg_2 \frac{1}{p_i} = -\lg_2 p_i = \lg_2 W_i \tag{11.6}$$

where p_i is defined from the Boltzmann distribution as:

$$p_i = \frac{\exp(-E_i/kT)}{\sum_{m=0}^{\infty} \exp(-n_m h\nu_i/kT)} \tag{11.7}$$

where n_m is quantum number; h is the Plank constant; $E_i = h\nu_i$ is the energy of (i)-state.

There is strict relation between the entropy and information, leading from comparison of (11.6), (11.1 and 11.4):

$$S_i = (k_B \ln 2) I_i = 2.3 \cdot 10^{-24} I_i \tag{11.8}$$

The information entropy is given as expectation of the information in the system (Nicolis,1986; Haken, 1988).

$$< I >= \Sigma P_i \lg_2(1/p_i) = -\Sigma p_i \lg_2(p_i) \tag{11.9}$$

From (26) and (22) we can see that variation of probability p_i and/or N_i in (20) will lead to changes of entropy and information, characterizing the matter as a hierarchical system.

The **reduced information** (entropy), characterizing its **quality**, related to selected collective excitation of any type of condensed matter, we introduce here as a product of corresponding component of information $[I_i]$ to the number of molecules (atoms) with similar dynamic properties in composition of this excitation:

$$q_i = (v_i/v_m) = N_0/(V_0 n_i) \tag{11.9a}$$

where: $v_i = 1/n_i$ is the volume of quasiparticle, reversible to its concentration (n_i); $v_m = V_0/N_0$ is the volume, occupied by one molecule.

The product of (11.9) and (11.9a), i.e. the **reduced information** gives the quantitative characteristic not only about quantity but also about the quality of the information:

$$(Iq)_i = p_i \lg_2(1/p_i) \cdot N_0/(V_0 n_i) \tag{11.9b}$$

This new formula could be considered as a useful modification of known Shennon equation.

11.3. Experimentally revealed macroscopic oscillations

A series of experiments was conducted in our laboratory to study macroscopically coherent oscillations in the buffer (pH 7.3) containing 0.15 M NaCl as a control system and immunoglobulin G solutions in this buffer at the following concentrations: $3 \cdot 10^{-3}$; $6 \cdot 10^{-3}$; $1.2 \cdot 10^{-2}$ and $2.4 \cdot 10^{-2} mg/ml$.

The turbidity (D^*) of water and the solutions were measured every 10 seconds with the spectrophotometer at $\lambda = 350nm$. Data were obtained automatically with the time constant 5 s during 40 minutes. The number of D^* values in every series was usually equal to 256. The total number of the fulfilled series was more than 30.

The time series of D^* were processed by the software for time series analysis. The time trend was thus subtracted and the autocovariance function and the spectral density were calculated.

The empty quartz cuvette with the optical path about 1 cm were used as a base control.

Only the optical density of water and water dissolved substances, which really exceeded background optical density in the control series were taken into account. It is shown that the noise of the photoelectronic multiplier does not contribute markedly to dispersion of D^*.

The measurements were made at temperatures of 17, 28, 32, and 37^0. The period of the trustworthily registered oscillation processes related to changes in D^*, had 2 to 4 discrete values over the range of $(30 - 600)$ sec under our conditions. It does not exclude the fact that the autooscillations of longer or shorter periods exist. For example, in distilled water at 32^0C the oscillations of the scattering ability are characterized by periods of 30, 120 and 600 s and the spectral density amplitudes 14, 38 and 78 (in relative units), respectively. With an increase in the oscillation period their amplitude also increases. At 28^0C the periods of the values 30, 41 and 92 seconds see have the corresponding normalized amplitudes 14.7, 10.6 and 12.0.

Autooscillations in the buffer solution at 28^0C in a 1 cm wide cuvette with the optical way length 1 cm (i.e. square section) are characterized with periods: 34, 52, 110 and 240 s and the amplitudes: 24, 33, 27 and 33 relative units. In the cuvette with a smaller (0.5 cm) or larger (5 cm) optical wavelength at the same width (1 cm) the periods of oscillations in the buffer change insignificantly. However, amplitudes decreased by 50% in the 5 cm cuvette and by 10-20% in the 0.5 cm-cuvette. This points to the role of geometry of space where oscillations occur, and to the existence of the finite correlation radius of the synchronous processes in the volume. But this radius is macroscopic and comparable with the size of the cuvette.

The dependence of the autooscillations amplitude on the concentration of the protein - immunoglobulin G has a sharp maximum at the concentration of $1.2 \cdot 10^{-2}\, mg/ml$. There is a background for considering it to be a manifestation of the hydrodynamic Bjorkness forces between the pulsing macromolecules (Käiväräinen, 1987).

Oscillations in water and water solutions with nearly the same periods have been registered by the light-scattering method by Chernikov (1985).

Chernikov (1990d) has studied the dependence of light scattering fluctuations on temperature , mechanic perturbation and magnetic field in water and water hemoglobin and DNA solution. It has been shown that an increase in temperature results in the decline of long-term oscillation amplitude and in the increase of short-time fluctuation amplitude. Mechanical mixing removes long-term fluctuations and over 10 hours are spent for their recovery. Regular fluctuations (oscillations) appear when the constant magnetic field above $240 A/m$ is applied; the fluctuations are retained for many hours after removing the field. The period of long-term oscillations has the order of 10 minutes. It has been assumed that the maintenance of long-range correlation of molecular rotation-translation fluctuation underlies the mechanism of long-term light scattering fluctuations.

It has been shown (Chernikov, 1990b) that a pulsed magnetic field (MF), like constant MF, gives rise to light scattering oscillations in water and other liquids containing H atoms: glycerin, xylol, ethanol, a mixture of unsaturated lipids. All this liquids also have a distinct response to the constant MF. "Spontaneous" and MF-induced fluctuations are shown to be associated with the isotropic component of scattering. These phenomena do not occur in the nonproton liquid (carbon tetrachloride) and are present to a certain extent in chloroform (containing one hydrogen atom in its molecule). The facts obtained indicate an important role of hydrogen atoms and cooperative system of hydrogen bonds in "spontaneous" and induced by external perturbations macroscopic oscillations.

The understanding of such phenomena can provide a physical basis for of self-organization (Prigogin, 1980, 1984, Babloyantz, 1986), the biological system evolution (Shnol, 1979, Udaltsova et al., 1987), and chemical processes oscillations (Field and Burger, 1988).

It is quite probable that macroscopic oscillation processes in biological liquids, e.g. blood and liquor, caused by the properties of water are involved in animal and human physiological processes.

We have registered the oscillations of water activity in the protein-cell system by means of light microscopy using the apparatus "Morphoquant", through the change of the erythrocyte sizes, the erythrocytes being ATP-exhausted and fulfilling a role of the passive osmotic units. The revealed oscillations have a few minute-order periods.

Preliminary data obtained from the analysis of oscillation processes in the human cerebrospinal liquor indicate their dependence on some pathology. Perhaps, the autooscillations spectrum of the liquor can serve as a sensitive test for the physiological status of the organism. The liquor is an electrolyte and its autooscillations can be modulated with the electromagnetic activity of the brain.

The activity of the central nervous system and the biological rhythms of the organism may be dependent on the oscillation processes in the liquor. If it is the case, then the directed influence on these autooscil-

lation processes, for example, by means of external electromagnetic field of resonant frequency makes it possible to regulate the state of the organism. Such way of correction of biorhythms could be simple and effective.

During my stay in laboratory of G.Salvetty in the Institute of Atomic and Molecular Physics in Pisa (Italy) in 1992, the oscillations of heat capacity $[C_p]$ in 0.1 M phosphate buffer (pH7) and in 1% solution of lysozyme in the same buffer at 20^0C were revealed. The sensitive adiabatic differential microcalorimeter was used for this aim. The biggest relative amplitude changing: $[\Delta C_p]/[C_p] \sim (0.5\pm 0.02)\%$ occurs with period of about 24 hours, i.e. corresponding to circadian rhythm.

Such oscillations can be stimulated by the variation of magnetic and gravitational conditions of the Earth in location of experiment during this 24h cycle.

11.4. Phenomena in water and aqueous systems, induced by magnetic field

In the works of (Semikhina and Kiselev, 1988, Kiselev et al., 1988, Berezin et al., 1988) the influence of the weak magnetic field was revealed on the dielectric losses, the changes of dissociation constant, density, refraction index, light scattering and electroconductivity, the coefficient of heat transition, the depth of super-cooling for distilled water and for ice also. This field used as a modulator a geomagnetic action.

The absorption and the fluorescence of the dye (rhodamine 6G) and protein in solutions also changed under the action of weak fields on water. The latter circumstance reflects feedback links in the guest-host, or solute -solvent system.

The influence of constant and variable magnetic fields on water and ice in the frequency range $10^4 - 10^8 Hz$ was studied. The maximum sensitivity to field action was observed at the frequency $\nu_{\max} = 10^5 Hz$. In accordance with our calculations, this frequency corresponds to frequency of superdeformons excitations in water (see Fig..12.d).

A few of physical parameters changed after the long (nearly 6 hour) influence of the variable fields ($\tilde{\mathrm{H}}$), modulating the geomagnetic field of the tension $[H = H_{\mathrm{geo}}]$ with the frequency (f) in the range of $(1-10)\cdot 10^2 Hz$ (Semikhina and Kiselev, 1988, Kiselev et al., 1988):

$$H = H\cos 2\pi f t \tag{11.10}$$

In the range of modulating magnetic field (H) tension from 0.08 A/m to $212 A/m$ the **eight maxima of dielectric losses tangent** in the above mentioned (f) range were observed. Dissociation constant decreases more than other parameters (by 6 times) after the incubation of ice and water in magnetic field. The relaxation time ("memory") of the changes, induced in water by fields was in the interval from 0.5 to 8 hours.

The authors interpret the experimental data obtained as the influence of magnetic field on the probability of proton transfer along the net of hydrogen bonds in water and ice, which lead to the deformation of this net.

The *equilibrium constant* for the reaction of dissociation:

$$H_2O \Leftrightarrow OH^- + H^+ \tag{11.11}$$

in ice is less by almost six orders ($\simeq 10^6$) than that for water. On the other hand the values of the *field- induced effects in ice are several times more than in water*, and the time for reaching them in ice is less. So, the above interpretation is doubtful.

In the framework of our concept all the aforementioned phenomena could be explained by the shift of the $(a \Leftrightarrow b)$ **equilibrium of primary translational and librational effectons to the left.** In turn, this shift stimulates polyeffectons or coherent superclusters growth, under the influence of magnetic fields. Therefore, parameters such as the refraction index, dielectric permeability and light scattering have to enhance in-phase, while the H_2O dissociation constant depending on the probability of superdeformons must decrease. The latter correlate with declined electric conductance.

As far, the magnetic moments of molecules within the coherent superclusters or polyeffectons formed by primary librational effectons are additive parameters, then the values of changes induced by magnetic field must be proportional to polyeffectons sizes. These sizes are markedly higher in ice than in water and decrease with increasing temperature.

Inasmuch the effectons and polyeffectons interact with each other by means of phonons (i.e. the subsystem of secondary deformons), and the velocity of phonons is higher in ice than in water, then the saturation of all concomitant effects and achievement of new equilibrium state in ice is faster than in water.

The frequencies of geomagnetic field modulation, at which changes in the properties of water and ice have maxima can correspond to the eigen-frequencies of the $[a \Leftrightarrow b]$ equilibrium constant of primary effectons oscillations, determined by [assembly $\Leftrightarrow$ disassembly] equilibrium oscillations for coherent super clusters or polyeffectons.

The presence of dissolved molecules (ions, proteins) in water or ice can influence on the initial $[a \Leftrightarrow b]$ equilibrium dimensions of polyeffectons and,consequently the interaction of solution with outer field.

Narrowing of ^{1}H-NMR lines in a salt-containing water and calcium bicarbonate solution was observed after magnetic field action. This indicates that the degree of ion hydration is decreased by magnetic treatment. On the other hand, the width of the resonance line in *distilled water* remains unchanged after 30 minute treatment in the field (135 kA/m) at water flow rate of 60 cm/s (Klassen, 1982).

The hydration of diamagnetic ions (Li^+, Mg^{2+}, Ca^{2+}) decreases, while the hydration of paramagnetic ions (Fe^{3+}, Ni^{2+}, Cu^{2+}) increases. It leads from corresponding changes in ultrasound velocity in ion solutions (Duhanin and Kluchnikov, 1975).

There are numerous data which pointing to an increase the coagulation of different particles and their sedimentation velocity after magnetic field treatment. These phenomena provide a reducing the scale formation in heating systems, widely used in practice. Crystallization and polymerization also increase in magnetic field. It points to decrease of water activity.

Increasing of refraction index (n) of water and its dielectric permeability $(\epsilon \simeq n^2)$ **with in-phase enhancement of liquid viscosity (Mi-**

nenko, 1981) are in total accordance with our hierarchic viscosity theory.

It follows from our mesoscopic model that the increase of (n) is related to the increase of molecular polarizability (α) due to the shift of $(a \Leftrightarrow b)_{tr,lb}$ equilibrium of primary effectons leftward under the action of magnetic field. On the other hand, distant Van der Waals interactions and consequently dimensions of primary effectons depend on α. This explains the elevation of surface tension of liquids after magnetic treatment.

The leftward shift of $(a \Leftrightarrow b)_{tr,lb}$ equilibrium of primary effectons must lead to decreasing of water activity due to (n^2) increasing and structural factor (T/U_{tot}) decreasing its structure ordering. Corresponding changes in the vapor pressure, freezing, and boiling points, coagulation, polymerization and crystallization are the consequences of this shift and water activity decreasing.

It follows from our theory that any changes in condensed matter properties must be accompanied by change of such parameters as:

1) density;
2) sound velocity;
3) positions of translational and librational bands in oscillatory spectra;
4) refraction index.

Using our equations and computer simulations by means of elaborated computer program: Comprehensive Analyzer of Matter Properties (CAMP), it is possible to obtain from these changes very detailed information (more than 250 parameters) about even small perturbations of matter on meso- and macroscopic levels.

Available experimental data indicate that all of above mentioned 4 experimental parameters of water have been changed indeed after magnetic treatment. Minenko (1981) has shown that bidistilled water *density* increases by about 0.02% after magnetic treatment (540 kA/m, flow rate 80 cm/s). *Sound velocity* in distilled water increases to 0.1% after treatment under conditions: 160 kA/m and flow rate 60 $cm/$s.

The *positions of the translational and librational bands* of water were also changed after magnetic treatment in $415kA/m$ (Klassen, 1982).

11.5. Coherent radio-frequency oscillations in water, revealed by C. Smith

It was shown experimentally by Smith (1994) that the water display a coherent properties in macroscopic scale and memory. He shows that water is capable of retaining the frequency of an alternating magnetic field. For a tube of water placed inside a solenoid coil, the threshold for the alternating magnetic field, potentiating electromagnetic frequencies into water, is 7.6 μT (rms). He comes to conclusion that the frequency information is carried on the magnetic vector potential.

He revealed also that in a course of yeast cells culture synchronously dividing, the radio-frequency emission around 1 MHz ($10^6\,1/s$), 7-9 MHz (7-$9\times10^6\,1/s$) and 50-80 MHz (5-$9\times10^7 1/s$) with very narrow bandwidth (˜50 Hz) might be observed for a few minutes.

These frequencies could correspond to frequencies of different water collective excitations, introduced in our Hierarchic theory, like [lb/tr] macroconvertons,

the $[a \rightleftharpoons b]_{lb}$ transitons, etc. (see Fig. 12), taking into account the deviation of water properties in the colloid and biological systems as respect to pure one.

Cyril Smith has proposed that the increasing of coherence radius in water could be a consequence of coherent water clusters association due to Josephson effect (Josephson, 1965): tunneling of molecules between clusters. As far primary librational effectons are resulted from partial Bose-condensation of molecules, this idea looks quite acceptable in the framework of our Hierarchic theory.

The coherent macroscopic oscillations in tube with water, revealed by C.Smith could be induced by coherent electromagnetic radiation of microtubules of cells, produced by correlated intra-MTs water excitations in accordance with our Hierarchic model of consciousness (see Kaivarainen, 1998 and "New Articles" in homepage: http://www.karelia.ru/~alexk).

The biological effects of magnetically treated water can have very important applications. For example, hemolysis of erythrocytes is more vigorous in magnetically pretreated physiological solutions (Trincher, 1967). Microwave radiation induces the same effect (Il'ina et al., 1979). But after boiling such effects in the treated solutions have been disappeared. It is shown that magnetic treatment of water strongly stimulates the growth of corn and plants (Klassen, 1982).

Now it is obvious that a systematic research program is needed to understand the physical background of multilateral effects of magnetized water.

11.6. Influence of weak magnetic field on the properties of solid bodies

It has been established that as a result of magnetic field action on solids with interaction energy ($\mu_B H$) much less than kT, many properties of matter such as hardness, parameters of crystal cells and others change significantly.

The short-time action of magnetic field on silicon semiconductors is followed by a very long (many days) relaxation process. The action of magnetic field was in the form of about 10 impulses with a length of 0.2 ms and an amplitude of about $10^5 A/\mathrm{m}$. The most interesting fact was that this relaxation had an oscillatory character with periods of about several days (Maslovsky and Postnikov, 1989).

Such a type of long period oscillation effects has been found in magnetic and nonmagnetic materials.

This points to the general nature of the macroscopic oscillation phenomena in solids and liquids.

The period of oscillations in solids is much longer than in liquids. This may be due to stronger deviations of the energy of (a) and (b) states of primary effectons and polyeffectons from thermal equilibrium and much lesser probabilities of transiton and deformon excitation. Consequently, the relaxation time of $(a \Leftrightarrow b)_{tr,lb}$ equilibrium shift in solids is much longer than in liquids. The oscillations originate due to instability of dynamic equilibrium between the subsystems of effectons and deformons.

11.7. Possible mechanism of perturbations of nonmagnetic materials under magnetic treatment

We shall try to discuss the interaction of magnetic field with diamagnetic matter like water as an example. The magnetic susceptibility (χ) of water is a sum of two opposite contributions (Eisenberg and Kauzmann, 1969):

1) average negative diamagnetic part, induced by external magnetic field:

$$\bar{\chi}^d = \frac{1}{2}(\chi_{xx} + \chi_{yy} + \chi_{zz}) \cong -14.6(\pm 1.9) \cdot 10^{-6} \tag{11.12}$$

2) positive paramagnetism related to the polarization of water molecule due to asymmetry of electron density distribution, existing without external magnetic field. Paramagnetic susceptibility (χ^p) of H_2O is a tensor with the following components:

$$\chi^p_{xx} = 2.46 \cdot 10^{-6}; \quad \chi^p_{yy} = 0.77 \cdot 10^{-6}; \quad \chi^p_{zz} = 1.42 \cdot 10^{-6} \tag{11.13}$$

The resulting susceptibility:

$$\chi_{H_2} = \bar{\chi}^d + \bar{\chi}^p \cong -13 \cdot 10^{-6} \tag{11.14}$$

The second contribution in the magnetic susceptibility of water is about 10 times lesser than the first one. But the first contribution to the magnetic moment of water depends on external magnetic field and must disappear when it is switched out in contrast to second one.

The coherent primary librational effectons of water even in liquid state contain about 100 molecules $\left[(n^{ef}_M)_{lb} \simeq 100\right]$ at room temperature (Fig.4a). In ice $(n^{ef}_M)_{lb} \geq 10^4$. In (a)-state the vibrations of all these molecules are synchronized in the same phase, and in (b)-state - in counterphase. Correlation of H_2O forming effectons means that the energies of interaction of water molecules with external magnetic field are additive:

$$\epsilon^{ef} = n^{ef}_M \cdot \mu_p H \tag{11.15}$$

In such a case this total energy of effecton interaction with field may exceed thermal energy:

$$\epsilon^{ef} > kT \tag{11.16}$$

In the case of polyeffectons formation this inequality becomes much stronger.

It follows from our model that interaction of magnetic field with (a)-state of the effectons must be stronger than that with (b)-state due to the additivity of the magnetic moments of coherent molecules:

$$\epsilon_a^{ef} > \epsilon_b^{ef} \tag{11.17}$$

Consequently, magnetic field shifts $(a \Leftrightarrow b)_{tr,lb}$ equilibrium of the effectons leftward. At the same time it minimizes the potential energy of matter, because potential energy of (a)-state (V_a) is lesser than (V_b):

$$V_a < V_b \quad \text{and} \quad E_a < E_b, \tag{11.18}$$

where $E_a = V_a + T^a_{\text{kin}}$; $E_b = V_b + T^b_{\text{kin}}$ are total energies of the effectons.

We keep in mind that the kinetic energies of (a) and (b)-states are equal: $T^a_{\text{kin}} = T^b_{\text{kin}} = p^2/2m$.

These energies decreases with increasing of the effectons dimensions, determined by the most probable impulses in selected directions:

$$\lambda_{1,2,3} = h/p_{1,2,3}$$

The energy of interaction of magnetic field with deformons as a transition state of effectons must be even less than ϵ_b^{ef} due to lesser order of molecules in this state and reciprocal compensation of their magnetic moments:

$$\epsilon_d < \epsilon_b^{ef} \leq \epsilon_a^{ef} \tag{11.19}$$

This important inequality means that as a result of external magnetic field action the shift of $(a \Leftrightarrow b)_{tr,lb}$ leftward is reinforced by leftward shift of equilibrium [effectons $\rightleftharpoons$ deformons] subsystems of matter.

If water is flowing in a tube it increases the relative orientations of all effectons in volume and stimulate the coherent superclusters formation. All the above discussed effects must increase. Similar ordering phenomena happen in a rotating tube with liquid.

After switching off the external magnetic field the relaxation of *induced ferromagnetism* in water begins. It may be accompanied by the oscillatory behavior of $(a \Leftrightarrow b)_{tr,lb}$ equilibrium. All the experimental effects discussed above can be explained as a consequence of orchestrated in volume $(a \Leftrightarrow b)$ equilibrium oscillations.

Remnant ferromagnetism in water was experimentally established using a SQUID superconducting magnetometer by Kaivarainen et al. in 1992 at Physical department of University of Turku (unpublished data).

In these experiments water was treated in constant magnetic field $50G$ for two hours. Then it was frozen and after switching off external magnetic field the remnant ferromagnetism was registered at helium temperature. Even at this low temperature the slow relaxation of ferromagnetic signal amplitude was revealed. These results point to the correctness of the proposed mechanism of magnetic field - water interaction and perturbation. In the future this mechanism can be developed to quantitative level.

The attempt to make a theory of magnetic field influence on water based on other model were made already (Yashkichev, 1980). However, this theory does

not take into account the quantum properties of water and cannot be considered as a complete one.

The comprehensive material obtained by group of S. Shnol (1987, 1998) when studying macroscopic oscillations of very different nature reveals their fundamental character and their dependence on gravitational coherent global perturbations.

For more detailed discussion of like phenomena see my article: Dynamic model of wave-particle duality, Bi-vacuum and Superunification", placed at http://arxiv.org/abs/physics/0003001

12. INNOVATION, BASED ON NEW THEORY:
Comprehensive Analyzer of Matter Properties (CAMP)
[see: www.karelia.ru/~alexk (CAMP)]

The set of formulae obtained in our theory allows to calculate about 300 parameters of any condensed matter (liquid or solid). Most of them are hidden, i.e. inaccessible for direct experimental measurements.

Simulations evaluation of these parameters can be done using our computer program: CAMP (copyright 1997) and the following experimental methods:

1. Far-middle IR spectroscopy for determination the positions of translational or librational bands: (30-2500) cm-1;
2. Sound velocimetry;
3. Dilatometry or densitometry, for molar volume or density registration;
4. Refractometry.

Corresponding data should be obtained simultaneously at the same temperature and pressure from the SAME SAMPLE in ideal case. Among the parameters of matter evaluated are so important as: internal energy, heat capacity, thermal conductivity, viscosity, coefficient of self-diffusion, surface tension, solvent activity, vapor pressure, internal pressure, parameters of all types of quasiparticles (concentration, volume, dimensions, energy, probability of excitation, life-time) and many others.

This leads to idea of new optoacoustic device: Comprehensive Analyzer of Matter Properties (CAMP), which may provide a huge amount of data of any condensed system under study. The most complicated and expensive component of CAMP is FT-IR spectrometer for far and middle region. The most sensitive parameter is sound velocity. The less sensitive and stable parameter is molar volume or density.

One of possible CAMP configuration should include special attachment to FT-IR spectrometer, making it possible registration of reflection spectra in far/middle IR region. Such approach allows to study the properties of samples with strong IR absorption (i.e. aqueous systems) and non transparent mediums. The combination of modified FT-IR spectrometer with other equipment for simultaneous measurement of matter density and sound velocity and refraction index will provide 4 parameters, necessary for CAMP function. The sample cell for liquids and solids should have a shape, convenient to make all these measurements simultaneously.

The another configuration of CAMP may include except FT-IR, the Brillouin light scattering spectrometer. It makes possible simultaneous measurement of

sound velocity (from the Doppler shift of side bands of Brillouin spectra) and positions of intermolecular bands [tr and lb] in oscillatory spectra in the far IR. Our hierarchic theory of Brillouin light scattering gives much more information about condensed matter properties than conventional one.

The interface of CAMP with personal computer will allow monitoring of very different dynamic physical process in real time, using our computer program.

Possible Applications for Comprehensive Analyzer of Matter Properties (CAMP)

Applications to aqueous systems

1. Monitoring of drinking water and water based beverage physical properties, related to taste and biological activity;
2. Monitoring of electromagnetic and acoustic pollution, using physical properties of water as a test system (ecology problem);
3. In pharmaceutical technology - for monitoring of water perturbations, induced by vitamins and drugs at low physiologic concentrations. Correlation of water structure perturbations, induced by vitamins, drugs, physical fields, with healing activity of solutions;
4. Study of colloid systems, related to paper technology. Monitoring of influence of electromagnetic and acoustic fields on physical parameters of the bulk and hydrated water for regulation of [coagulation - peptization] equilibrium of colloids, affecting the quality of paper;
5. In biotechnology and biochemistry: a wide range of problems, related to role of water in biosystems and water biopolymers interaction (i.e. mechanism of cryoproteins action);
6. Mechanism of transition of flow from the laminar to turbulent one in pipe-lines and the ways of this process regulation by means of electromagnetic and acoustic fields;
7. Evaluation of frequencies of cavitational fluctuations of water for the end of their effective resonant stimulation. It may be useful for: a) de-infection of drinking water; b) stimulation of sonoluminiscense; c) development of pure energy technology; d) cold fusion stimulation.

Application to nonaqueous systems

1. Fundamental research in all branches of condensed matter physics: thermodynamics, dynamics, phase transitions, transport process, surface tension, self-diffusion, viscosity, vapor pressure, etc.
2. Monitoring of new materials technology for searching the optimal conditions (T, P, physical fields) for providing the optimal parameters on mesoscopic and macroscopic scale for their best quality;
3. Study of mechanism of high-temperature superconductivity;
4. Study of mechanism of superfluidity.

Comprehensive Analyzer of Matter Properties (CAMP) represents a basically new type of scientific equipment, allowing to get incomparable big amount of information concerning physics of liquids or solids. It can be very useful for investigation of dynamics and mesoscopic structure of pure matter as well as solid and liquid solutions, the colloid systems and host-guest systems.

The market for Comprehensive Analyzer of Matter Properties (CAMP) is free and due to its unique informational potential could be much bigger than that for IR, Raman or Brillouin spectrometers.

CONCLUSION

A quantum based new hierarchic quantitative theory, general for solids and liquids, has been developed. It is assumed, that anharmonic oscillations of particles in any condensed matter lead to emergence of three-dimensional (3D) superposition of standing de Broglie waves of molecules, electromagnetic and acoustic waves. Consequently, any condensed matter could be considered as a gas of 3D standing waves of corresponding nature. Our approach unifies and develops the Einstein's and Debye's models.

Collective excitations, like 3D standing de Broglie waves of molecules, representing at certain conditions the molecular Bose condensate, were analyzed, as a background of hierarchic model of condensed matter.

The most probable de Broglie wave (wave B) length is determined by the ratio of Plank constant to the most probable impulse of molecules, or by ratio of its most probable phase velocity to frequency. The waves B of molecules are related to their translations (tr) and librations (lb).

As the quantum dynamics of condensed matter is anharmonic and does not follow the classical Maxwell-Boltzmann distribution, the real most probable de Broglie wave length can exceed the classical thermal de Broglie wave length and the distance between centers of molecules many times.

This makes possible the atomic and molecular mesoscopic Bose condensation in solids and liquids at temperatures, below boiling point. It is one of the most important results of new theory, which we have confirmed by computer simulations on examples of water and ice and applying to Virial theorem.

Four strongly interrelated new types of quasiparticles (collective excitations) were introduced in our hierarchic model:

1. *Effectons (tr and lb)*, existing in "acoustic" (a) and "optic" (b) states represent the coherent clusters in general case**;**

2. *Convertons*, corresponding to interconversions between *tr* and *lb* types of the effectons (flickering clusters);

3. *Transitons* are the intermediate $[a \rightleftharpoons b]$ transition states of the *tr* and *lb* effectons;

4. *Deformons* are the 3D superposition of IR electromagnetic or acoustic waves, activated by *transitons* and *convertons.*

Primary effectons (*tr and lb)* are formed by 3D superposition of the **most probable standing de Broglie waves** of the oscillating ions, atoms or molecules. The volume of effectons (tr and lb) may contain from less than one, to tens and even thousands of molecules. The first condition means validity of **classical** approximation in description of the subsystems of the effectons. The second one points to **quantum properties of coherent clusters due to mesoscopic Bose condensation (BC), in contrast to macroscopic BC, pertinent for superfluidity and supercoductivity**.

The liquids are semiclassical systems because their primary (tr) effectons contain less than one molecule and primary (lb) effectons - more than one

molecule. *The solids are quantum systems totally because both kind of their primary effectons (tr and lb) are mesoscopic molecular Bose condensates.* **These consequences of our theory are confirmed by computer simulations.**

The 1st order [$gas \rightarrow liquid$] transition is accompanied by strong decreasing of number of rotational (librational) degrees of freedom due to emergence of primary (lb) effectons and [$liquid \rightarrow solid$] transition - by decreasing of translational degrees of freedom due to Bose-condensation of primary (tr) effectons.

In the general case the effecton can be approximated by parallelepiped with edges determined by de Broglie waves length in three selected directions (1, 2, 3), related to symmetry of molecular dynamics. In the case of isotropic molecular motion the effectons' shape is approximated by cube.

The number of molecules in the volume of primary effectons (tr and lb) is considered as the "parameter of order" in our theory of 1st order phase transitions.

The in-phase oscillations of molecules in the effectons correspond to the effecton's (a) - *acoustic* state and the counterphase oscillations correspond to their (b) - *optic* state. States (a) and (b) of the effectons differ in potential energy only, however, their kinetic energies, impulses and spatial dimensions - are the same. **The b-state of the effectons has a common feature with Frölich's polar mode.**

The ($a \rightarrow b$) or ($b \rightarrow a$) transition states of the primary effectons (tr and lb), defined as primary transitons, are accompanied by a change in molecule polarizability and dipole moment without density fluctuations. At this case they lead to absorption or radiation of IR photons, respectively.

Superposition of three internal standing IR photons of different directions (1,2,3) - forms primary electromagnetic deformons (tr and lb).

On the other hand, the [$\mathrm{lb} \rightleftharpoons \mathrm{tr}$] *convertons* and *secondary transitons* are accompanied by the density fluctuations, leading to absorption or radiation of phonons.

Superposition of standing phonons in three directions (1,2,3), forms **secondary acoustic deformons (tr and lb).**

Correlated collective excitations of primary and secondary effectons and deformons (tr and lb), localized in the volume of primary tr and lb electromagnetic deformons, lead to origination of **macroeffectons, macrotransitons** and **macrodeformons** (tr and lb respectively)**.**

Correlated simultaneous excitations of tr and lb macroeffectons in the volume of superimposed *tr* and *lb* electromagnetic deformons lead to origination of **supereffectons.**

In turn, the simultaneous excitation of **both***: tr* and *lb macrodeformons and macroconvertons* in the same volume means origination of **superdeformons.** Superdeformons are the biggest (cavitational) fluctuations, leading to microbubbles in liquids and to local defects in solids.

Total number of quasiparticles of condensed matter equal to 4!=24, reflects all of possible combinations of the four basic ones [1-4], introduced above. This set of collective excitations in the form of "gas" of 3D standing waves of three types: de Broglie, acoustic and electromagnetic - is shown to be able to explain virtually all the properties of all condensed matter.

The important positive feature of our hierarchic model of matter is that it does not need the semi-empiric intermolecular potentials for calculations, which

are unavoidable in existing theories of many body systems. The potential energy of intermolecular interaction is involved indirectly in dimensions and stability of quasiparticles, introduced in our model.

The main formulae of theory are the same for liquids and solids and include following experimental parameters, which take into account their different properties:

[1]- Positions of (tr) and (lb) bands in oscillatory spectra;

[2]- Sound velocity;

[3]- Density;

[4]- Refraction index.

The knowledge of these four basic parameters at the same temperature and pressure makes it possible using our computer program, to evaluate more than 300 important characteristics of any condensed matter. Among them are such as: total internal energy, kinetic and potential energies, heat-capacity and thermal conductivity, surface tension, vapor pressure, viscosity, coefficient of self-diffusion, osmotic pressure, solvent activity, etc. Most of calculated parameters are hidden, i.e. inaccessible to direct experimental measurement.

This is the first theory able to predict all known experimental anomalies for water and ice. The conformity between theory and experiment is very good even without adjustable parameters.

The hierarchic concept creates a bridge between micro- and macro- phenomena, dynamics and thermodynamics, liquids and solids in terms of quantum physics.

Computerized verification of our Hierarchic theory of matter on examples of water and ice has been performed, using special computer program: Comprehensive Analyzer of Matter Properties (CAMP, copyright, 1997, Kaivarainen). The new optoacoustic device (CAMP), based on this program, with possibilities much wider, than that of IR, Raman and Brillouin spectrometers, has been proposed by the author (see URL: http://www.karelia.ru/˜alexk [CAMP]).

The demo (free) and commercial version of program are available and may be ordered.

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